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ERRATA.

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Line  
16, 6° } for "2-Methyl-1:3-benzoxazine-4-one" read  
11, 8°, 15° } "2-Methyl-1:3-dihydrobenzoxazine-4-one."  
10° alter formula to " $N_2CH \begin{smallmatrix} N \\ \diagup \\ N \end{smallmatrix}$ ".

in head-line \* for "NITROGEN" read "HYDROGEN."

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2° for "much less" read "much more."

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\* From bottom.



## I.—Note on Gynocardin and Gynocardase.

Gustavus Wilson Moore and Frank Tutin.

Gynocardin, a glucoside, gynocardin was first isolated by Power (Proc., 1904, 20, 137) from the seeds of *Gynocardia* Br., and has more recently been obtained by A. W. K. (the Journal of Pharmacy, Mainz, (Zoo. tier. chim.,

and Lees (Trans., 1905, 37, 119) have shown that gynocardin has the formula  $C_{12}H_{14}O_7N$ , and that it undergoes according to the following equation:



The mentioned investigators, however, found that, of the products, only dextrose and hydrogen cyanide could be isolated, the other product spontaneously recombined. The present authors thought that some further information on the unknown hydrolytic product of gynocardin might be obtained by methylating gynocardinic acid (Power and Lees, *loc. cit.* according to Purdie and Pitkeathly's method (Trans., 1899, 1) and subsequently hydrolysing the methylated product. The object in view has not been achieved, some new experiments regarding gynocardin have been made which are of some interest.

On the methylation of gynocardinic acid, a liquid methyl gynocardate was obtained which could be distilled without decomposition, and, on analysis, gave figures corresponding to the formula  $C_{12}H_{14}O_4(OMe)_2.CO_2Me$ . The yield of this was, however, small, and no definite hydrolytic product was obtained from it.

Gynocardin has been found to possess feebly acidic properties, being feebly acid to litmus, and yields with sodium ethoxide or potassium hydroxide a sodium derivative,  $C_{12}H_{14}O_7NNa$ .

It has been shown by Power and Lees (*loc. cit.*) that gynocardin is soluble only with difficulty, and the present authors have shown that this might be owing to the fact that gynocardin is a cyanide, since E. F. Armstrong (Proc. Roy. Soc., 1904, 74, 1) has shown that such compounds undergo hydrolysis by means of mineral acids more slowly than do their  $\beta$ -isomerides. Comparative experiments have now shown that, whereas gynocardin is rapidly hydrolysed by the enzyme gynocardase, which is present in the seeds, it is comparatively indifferent towards

The converse of this is the case with amygdalin, this being only very slowly hydrolysed by gynocardase.

The behaviour of gynocardase towards salicin and man then investigated, when it was ascertained that this enzyme only an extremely slow hydrolysis of the glucoside, but lute without action on maltose. The effect of di gynocardin was then examined, and it was observed enzyme was quite devoid of action on the glucoside in thus differing from emulgin, which does hydrolyse gyn although only to a very minor extent.

When, however, the respective effects of gynocardase an on *l*-mandelonitrile glucoside were investigated, it was fo in this case, the two enzymes possessed practically equal ac

It is evident, therefore, that the glucoside, gynocardin, enzyme, gynocardase, must both belong to the  $\beta$ -series, standing the fact that emulgin is almost indifferent gynocardin, and that gynocardase has only a very slight amygdalin.

Quantitative experiments have also shown that the hydrolysis of gynocardin by acids, although very considerable than that of salicin, is actually greater than that of amygdal

It would appear, therefore, that gynocardin and gynoc are analogous in their behaviour to phascolumatin and it sponding enzyme, which were originally assigned by Dunst Henry (*Proc. Roy. Soc.*, 1903, **72**, 285) to the  $\alpha$ -series, b quite recently been shown by H. E. Armstrong and E. (*ibid.*, 1910, **28**, B, 349) to belong to the  $\beta$ -series.

The fact that the enzyme from *Phaseolus lunatus* seeds active towards *l*-mandelonitrile glucoside, whilst it exerts very minor action on amygdalin, was attributed by Armstrong (*loc. cit.*) to the inhibiting action of the second molecule in the last-mentioned compound. Gynocardase, h although behaving quite analogously to phascolumatase with to amygdalin and *l*-mandelonitrile glucoside, only cau extremely slow hydrolysis of salicin. It is evident, therfore the nature of the non-glucose part of the molecule of a g may also exert a considerable influence with regard to ceptibility of such a compound to the action of enzymes.

#### EXPERIMENTAL

##### Methylation of Gynocardinic Acid.

Gynocardinic acid was prepared by the action of hot hydroxide on gynocardin, when ammonia is evolved and gynocardinate formed (Power and Lees, *loc. cit.*). The gynocardinate thus obtained is a readily soluble salt, from the gynocardinic acid may be prepared by exactly precip

with sulphuric acid. It was observed by the present author when a considerable excess of barium hydroxide is added to the hydrolysis a very sparingly soluble crystalline compound of barium gynocardinate and barium hydroxide is formed, but this was not further investigated.

Grams of gynocardinic acid were methylated by means of methyl iodide and dry silver oxide according to Purdie and Purdie's method (*loc. cit.*). The methylation was first carried out in ethyl alcohol solution, and was repeated under these conditions when the product was soluble in methyl iodide, after which the methylation was effected in methyl iodide solution, the reaction being continued until there was no further reaction on addition of dry silver oxide. The methylated product was removed from the reaction mixture by means of ether. It formed a thick oil which showed no signs of crystallising. When distilled under diminished pressure, a definite fraction boiling at 100° was obtained, which formed a viscid liquid at the ordinary temperature:

gave 0.3170 CO<sub>2</sub> and 0.1145 H<sub>2</sub>O. C = 52.6; H = 7.7.

C<sub>13</sub>H<sub>22</sub>O<sub>11</sub> requires C = 52.3; H = 7.3 per cent.

Determination of the number of methoxyl groups by Perkin's modification of Zeisel's method gave the following result:

gave 0.6010 AgI, OMe = 42.2.

C<sub>13</sub>H<sub>22</sub>O<sub>5</sub>(OMe)<sub>6</sub> requires OMe = 42.6 per cent.

The substance is therefore a *methyl pentamethylgynocardinate*, (OMe)<sub>5</sub>.CO<sub>2</sub>Me, and must therefore still contain two hydroxyl groups, since Power and Lees have shown that gynocardin is a hepta-acetyl derivative. In the endeavour to obtain a fully acetylated product, a small quantity of the ester was heated with acetyl iodide and dry silver oxide for some hours at 100° in a test-tube, but the product gave practically the same results on analysis as before this treatment.

Heating methyl pentamethylgynocardinate with dilute sodium hydroxide, it was completely decomposed, nothing but brown, insoluble products resulting.

#### *Sodium Derivative of Gynocardin, C<sub>13</sub>H<sub>18</sub>O<sub>5</sub>NNa.*

As already mentioned, gynocardin possesses feebly acidic properties, the virtue of which it is able to form derivatives with the alkalis. On adding excess of sodium ethoxide or aqueous sodium hydroxide to an ethyl-alcoholic solution of gynocardin, a precipitate is produced, readily soluble in water, but not so readily in ethyl alcohol:

0.4140 gave 0.0635  $\text{Na}_2\text{CO}_3$   $\text{Na} = 6.6$ .

$\text{C}_{22}\text{H}_{22}\text{O}_7\text{NNa}$  requires  $\text{Na} = 6.5$  per cent.

Attempts to prepare methyl gynocardin from the derivative were unsuccessful.

*Action of Gynocardase and Emulsin on Gynocardin and Glucosides.*

As stated above, gynocardin is but slowly hydrolysed by dilute mineral acids, although this change is rapidly effected by means of the enzyme, gynocardase, which was obtained from *Gynocardia* seeds by Power and Lees (*loc. cit.*). Amygdalin, on the other hand, is only very slowly acted upon by gynocardase, action requiring about twelve hours before any benzaldehyde or hydrogen cyanide can be detected. The effect of gynocardase on gynocardin and amygdalin has therefore been studied quantitatively. In each case 0.5 gram of the glucoside dissolved in 50 c.c. of water and 0.2 gram of enzyme added, the mixture being allowed to remain for thirty minutes at  $25^\circ$ . The hydrogen cyanide was then removed by a current of air, and estimated by titration with silver nitrate in presence of potassium chloride, in the usual manner.

The results of these experiments are shown in the following table:

Enzyme.	Glucoside.	Volume of 1/10- AgNO <sub>3</sub> required.	Per cent of hydro- cyanide
Gynocardase.....	Gynocardin.....	4.0 c.c.	8
Gynocardase....	Amygdalin.....	0.1 "	none
Emulsin.....	Gynocardin.....	0.1 "	"
Emulsin.....	Amygdalin.....	4.8 "	8

The effect of the two enzymes in question on salicin was also investigated, and for this purpose one gram of the glucoside dissolved in 100 c.c. of water, and 0.5 gram of the respective enzyme added. The mixture was then allowed to remain at  $20^\circ$  for thirty minutes, after which the saligenin formed was isolated by extraction with ether, and weighed. The results obtained were as follows:

One gram of salicin, on treatment with gynocardase, gave 0.12 gram of saligenin. Percentage of glucoside hydrolysed = 1.2.

One gram of salicin, on treatment with emulsin, gave 0.48 gram of saligenin. Percentage of glucoside hydrolysed = 4.8.

The relative activity of emulsin and gynocardase on *l*-mandelonitrile glucoside was ascertained in the following manner. A sufficient supply of the pure glucoside not being obtainable, an extract of the bark of *Prunus serotina*, Ehrhart, was used, as this has been shown to contain *l*-mandelonitrile glucoside (Moore and Moore, *Trans.*, 1909, 95, 243). One hundred cc.

red bark were brought into 5 litres of boiling water, boiled for some time, and then filtered. The filtrate was under diminished pressure to 200 c.c., and then divided into two equal portions, to one of which 0.4 gram of *Salicin* was added, and to the other the same amount of *Gynocardin*. Each of the mixtures was then kept for thirty minutes, the liberated hydrogen cyanide was estimated as before. It was then found that the portion treated with *Salicin* required, on titration, 1.6 c.c. of *N/10* silver nitrate to produce a permanent turbidity, whilst the other mixture, treated with *Gynocardin*, required an almost identical amount, c.c.

*Hydrolysis of Gynocardin, Amygdalin, and Salicin.*

Relative rates of hydrolysis by acids of *Gynocardin*, *Amygdalin*, and *Salicin* were estimated quantitatively, as follows. Equal quantities of the three glucosides (1.00, 1.32, and 1.64 respectively) were boiled with 200 c.c. of a 2 per cent. solution of sulphuric acid. In the case of the two cyanoglucosides, steam was passed through the mixture for two hours, liquid being maintained at practically a constant volume, the hydrogen cyanide in the distillate was estimated in the usual manner. In the case of *Salicin* the mixture was heated for two hours in a flask attached to a reflux condenser, and the saligenin was estimated by means of ether, and weighed. It was thus found that, under analogous conditions, the extent to which these three were hydrolysed was as follows: *Gynocardin*, 6.5 per cent.; *Amygdalin*, 5.0 per cent.; *Salicin*, 78.7 per cent.

*Gynocardin* was dissolved in water, and diastase was added. Even after ten days, no hydrogen cyanide was developed. On treating maltose with *Gynocardase* for twenty-four hours, no change occurred, for, on subsequently converting the maltose into maltone, the product was found to consist solely of maltone.

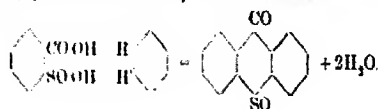


CXVII.—*New Syntheses of Thioxanthone and its Derivatives.*

By ERIC GIBSON DAVIS and SAMUEL SMILES.

THE experiments described in this paper were the outcome of a desire to study certain of the oxidation products of thioxanthene; but with this object in view it was necessary to obtain a considerable quantity of that substance. The preparation of thioxanthene by the method hitherto followed is somewhat tedious, since it involves the isolation of certain intermediate products, and the yield obtained leaves much room for improvement in the process. This synthesis of thioxanthene was devised by Graebe and Schulthess (*Annalen*, 1891, 263, 1); it consists in the removal of the elements of water from *o*-phenylthiolbenzoic acid,  $C_6H_4 \cdot S \cdot C_6H_4 \cdot CO_2H$ , by means of hot sulphuric acid. The yields of thioxanthene obtained from this reaction are good, but the crucial point of the synthesis is the production of the carboxylic acid. Graebe and Schulthess (*loc. cit.*) prepared the latter substance by the interaction of 5 g. mercaptan and the *o*-diazonium chloride of benzoic acid in a dilute solution, but since the introduction of *o*-thiolbenzoic acid as a cheap commercial product (Kalle & Co., D.R.-P. 204,450 (1908), F. Mayer (*Ber.*, 1909, 42, 1134) has improved Graebe and Schulthess's process by heating the methyl ester of the acid with sodium ethoxide, bromobenzene, and copper powder, to  $160^\circ$  for four hours. The yield of *o*-phenylthiolbenzoic acid obtained by this method was about 50 per cent.

In order to avoid the isolation of these intermediate products, we have employed *o*-carboxybenzenesulphinic acid, which is readily obtained from anthranilic acid by the process devised by Gattermann (*Ber.*, 1899, 32, 1144), or by the reduction of the dichloride of *o*-carboxybenzenesulphonyl chloride.\* In previous papers (Smiles and Le Rougnol, *Trans.*, 1906, 89, 700) it has been shown that sulphinic acids readily condense with aromatic compounds in presence of dehydrating agents, yielding the corresponding sulphoxides, and it has now been found that the sulphinic acid in question undergoes this reaction. If, however, the condensation is carried out in the presence of hot concentrated sulphuric acid, the carboxyl group also takes part in the reaction, and the thioxanthone is immediately produced, for example, with benzene:

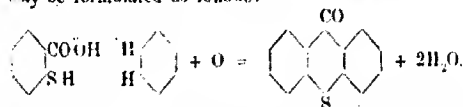


It may, however, be observed that, when dissolved in concentrated sulphuric acid, the sulphoxides are not stable in presence of a sulphinic acid, being reduced by the latter to sulphides (compare Smiles and Le Rossignol, *Trans.*, 1906, **89**, 707); hence the product which is isolated is not the sulphoxide formulated in the above equation, but is thioxanthone itself. In the case of the condensation of *o*-carboxybenzenesulphinic acid with benzene, the yield of thioxanthone is about 60 per cent. of that required by theory, and the fact that it does not more closely approach the theoretical is probably due to this instability of the sulphoxide. There is no doubt that the reduction of the sulphoxide takes place partly at the expense of the uncombined sulphinic acid, and the latter, being converted into the sulphonic acid, would then be prevented from undergoing the required condensation. In order to avoid this loss, we endeavoured to find a means by which the formation of the sulphoxide would be avoided.

Stenhouse (*Annalen*, 1869, **149**, 250; also Erlenmeyer and Lilenko, *Jahresber.*, 1861, 590) has shown that the mercaptans are rapidly oxidised by concentrated sulphuric acid, being converted into disulphides, thus:



Nothing is at present known of the mechanism of this reaction, and it seems to have been tacitly assumed that hydrogen is simultaneously removed by oxidation from two molecules of the mercaptan; there is, however, the alternative explanation that an oxygen derivative of the mercaptan is first formed, which then unites with the second molecule, forming the disulphide and one molecular proportion of water. The probability that, if the latter alternative is correct, this oxygen derivative of the mercaptan might be made to condense with aromatic nuclei justified the attempt to obtain thioxanthone by the interaction of *o*-thiolbenzoic acid and benzene in the presence of hot concentrated sulphuric acid. The result was successful, the yield under favourable conditions being as high as 90 per cent. of the theoretical. The reaction which takes place may be formulated as follows:



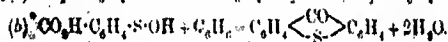
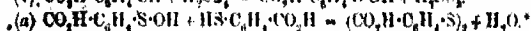
Experiments conducted with a wide range of material indicate that this method of preparing derivatives of thioxanthone is of general application; for, as might be anticipated from the behaviour of the parent substance, the majority of simple benzene derivatives furnish the corresponding thioxanthones.



very small quantity of *dithioisopropyl* acid is formed, the bulk of the product—about 90 per cent.—being thioxanthone.

(2) It may be observed that the formation of thioxanthone proceeds to a certain extent in sulphuric acid at about 20°, and it is difficult to imagine that aromatic hydrogen should be directly attacked by oxygen from that reagent under such conditions.

For these reasons we have rejected this hypothesis, and as an alternative adopt the only other which affords an adequate explanation: that the mercaptans are first oxidised by the sulphuric acid to an unstable oxygen derivative, which then unites with the aromatic complex or a second molecule of the mercaptan, water being eliminated under the influence of the condensing reagent. Further, adopting this explanation, it is evident that this intermediate compound must be one of the sulphonylic acids which have so often been assumed by chemists to be formed in the reactions of the lower oxidation products of organic sulphur compounds. The reactions in question would then be represented as follows:



It is true that no direct proof of the existence of these sulphonylic acids has yet been adduced either in these reactions or in any others in which they have been postulated, and in many other cases the evidence brought forward to warrant the assumption is very slender and open to other interpretation. However, in the present case there appears to us to be no satisfactory alternative. Further, it might be questioned whether the sulphonylic acid, even if it were formed, would undergo condensation with aromatic compounds, but in answer to this it may be observed that it has been already shown that hydroxyl attached to partly oxidised sulphur behaves in this manner (Smiles and Le Rossignol, *Trans.*, 1906, **39**, 696; 1908, **93**, 745); thus aromatic sulphinic acids and sulphoxide salts may be condensed in ice-cold sulphuric acid with aromatic compounds, giving triarylsulphonium salts, and even sulphur dioxide exhibits this reaction.

In summing up the case for the existence of the sulphonylic acid in the present reactions, it may be said that the alternative explanation is untenable, that all the available evidence is in its favour, and, whilst this is only of an indirect nature, there is none in contradiction.

With the view of throwing further light on this question, the

\* Considerable evidence may be adduced to show that, in concentrated sulphuric acid, this reaction is reversible; the question is at present under investigation.

reactions of the mercaptans and disulphides in concentrated sulphuric acid are now being studied, and attempts are being made to obtain derivatives of these sulphylic acids.

In the following pages are described the more important of the derivatives of thioxanthone which have been prepared by this method and it may be observed that at present the position of the substituents in the aromatic nuclei is uncertain. In view of the experiments which are being made by F. Mayer on other syntheses of these substances, we do not propose to follow up this question in detail.

#### EXPERIMENTAL.

With the object of synthesizing thioxanthone from *o*-carboxybenzenesulphonic acid it was necessary to obtain this acid in some quantity. It has already been prepared by Gattermann (*Ber.*, 1901, 32, 1111) by the interaction of *o*-carboxybenzenediazonium sulphate and sulphurous acid in the presence of copper powder; but in order to find the best method of preparing the acid, experiments were made with the alternative method of reducing *o*-carboxybenzenesulphonyl chloride. Preliminary experiments were made with the less expensive meta derivative.

##### *meta*-Carboxybenzenesulphonic Acid.

The dichloride of *meta*-carboxybenzenesulphonic acid was prepared according to the method described by Linpricht and Usler (*Ber.*, 1897, 102, 209), and it was reduced to the sulphonic acid by the following process. A saturated aqueous solution of sodium sulphite was warmed on the water bath, and the chloride was gradually added to this, the mixture being constantly shaken and kept alkaline during the course of the reaction. When all the chloride had dissolved, the contents of the flask were cooled, and then carefully acidified with concentrated sulphuric acid. The water part of the sulphonic acid was precipitated during this process but it was completely extracted from the mixture with ether. After the ethereal solution had been dried, it was distilled, and the residue was washed with benzene and recrystallised from water. Thirty-four grams of sulphonic acid were obtained from 1 gram of the chloride. A sample which had been dried in a vacuum desiccator was analysed:

0.2405 gave 0.3371  $\text{CO}_2$  and 0.0657  $\text{H}_2\text{O}$ .  $\text{C}=45.1$ ;  $\text{H}=3.04$ .

0.2442 " 0.3075  $\text{BaSO}_4$ .  $\text{S}=17.25$ .

1.2502 required 13.1 c.c. of 1.01*N*-KOH for neutralisation.

Equivalent = 94.7.

$\text{C}_6\text{H}_4\text{O}_3\text{S}$  requires  $\text{C}=45.17$ ;  $\text{H}=3.22$ ;  $\text{S}=17.2$  per cent.

Equivalent = 93.

When heated, the acid melts with profound decomposition, and the temperature at which this takes place depends somewhat on the rapidity of heating; under ordinary conditions it lies between  $196^{\circ}$  and  $200^{\circ}$ . Gattermann (*Ber.*, 1899, 32, 1144) gives  $197-198^{\circ}$  as the melting point. The substance is soluble in cold water and most organic media. That the compound is a sulphinic acid is shown by the production of a blue colour when treated with phenetole in concentrated sulphuric acid, and by the fact that it yields the normal type of product when treated with nitrous acid.

*Action of Nitrous Acid.*—A slight excess of sodium nitrite was dissolved in an aqueous solution of the sodium salt of the acid. Dilute sulphuric acid was then slowly added to the cooled mixture, when the required oximino-derivative immediately separated in the crystalline state. The yield was almost quantitative. The substance was collected, well washed with water, and finally crystallised from that medium containing a little nitrous acid:

0.7768 gave 26.1 c.c.  $N_2$  at  $18^{\circ}$  and 748 mm.  $N=3.9$ .

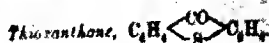
$C_{11}H_{11}O_6NS_2$  requires  $N=3.5$  per cent.

*Dicarboxybenzenesulphohydroximic acid* forms colourless prisms, which are soluble in hot water, and are slightly decomposed thereby. It is resolved into the components by cold aqueous alkali hydroxide, and on being gently warmed it evolves oxides of nitrogen.

#### *o*-Carboxybenzenesulphinic Acid.

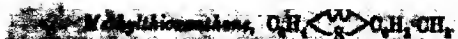
The stable dichloride (Remsen and Dolme, *Amer. Chem. J.*, 1889, 11, 340) of *o*-carboxybenzenesulphonic acid was prepared by the action of phosphorus pentachloride on the ammonium salt, and the product was reduced by the same process as applied to the meta-derivative. The results, however, were unsatisfactory, the yield of sulphinic acid being extremely poor and the process of isolation difficult. Moreover, the acid obtained, although agreeing in all other properties with that described by Gattermann (*Ber.*, 1899, 32, 1144), differs from this in the melting point given by that author. Gattermann states that the melting point of *o*-carboxybenzenesulphinic acid is  $125^{\circ}$ , but this is evidently a misprint, for on preparing the acid by the diazo-process we found that the product was identical with that yielded by the reduction method; both, when heated, assume a yellow colour at about  $200^{\circ}$ , and do not melt below  $270^{\circ}$ . A sample was recrystallised from glacial acetic acid, and then analysed. (Found,  $C=44.8$ ;  $H=3.5$ . Calc.,  $C=45.17$ ;  $H=3.22$  per cent.) Gattermann has shown, from the action of hydroxylamine on this substance, that it is a sulphinic acid, and we have further confirmed this structure by the behaviour

with phenoxide in concentrated sulphuric acid. In preparing this acid, the diazo process is to be recommended in preference to the reduction method, on account of the better yields. For 20 grams of anthranilic acid yielded about 18 grams of the sulphonic acid.



(a) *From o-carboxybenzenesulphonic Acid.*—Ten grams of *o*-carboxybenzenesulphonic acid were suspended in an excess of cold concentrated sulphuric acid, and excess of benzene was gradually added to the mixture, which was constantly shaken for about four hours. After the first addition of benzene the mixture assumed a deep blue colour, indicating the presence of a sulphonide; but this disappeared as the reaction proceeded, giving place to the strongly fluorescent, yellow solution of thioxanthone. At the same time sulphurous acid was evolved. The mixture was then set aside at the atmospheric temperature for a further nine hours, and was subsequently heated for one hour on the water-bath. The solution was poured on powdered ice, and the precipitate which formed was collected, washed with water, thoroughly triturated with 10 per cent aqueous alkali hydroxide, again collected, and finally washed with water until free from alkali. The dried substance was purified by extraction with chloroform in a Soxhlet apparatus; the extract was evaporated, and the residue was further purified by crystallisation from hot glacial acetic acid. The substance melted at  $209^\circ$ , and all other properties, such as colour, fluorescence, crystalline form, and solubility, agreed with those elsewhere attributed to thioxanthone. When mixed with thioxanthone from other sources, it melted at the same temperature. The yield of thioxanthone obtained by this process was about 60 per cent. of the theoretical, 7 grams being furnished by 10 grams of the sulphonic acid.

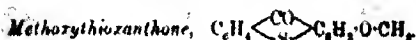
(b) *From o-thiolbenzoic Acid.*—The preparation of thioxanthone from *o*-thiolbenzoic acid was conducted in a similar manner and under the same conditions as that described in the foregoing paragraph. The reaction proceeds somewhat more energetically, sulphurous acid being continually evolved during the process. Ten grams of *o*-thiolbenzoic acid gave 12.5 grams of thioxanthone, or about 30 per cent. of that required by theory. After purification the substance melted at  $209^\circ$ . (Found, C=73.3; H=3.8; S=15.41. Calc., C=73.6; H=3.8; S=15.1 per cent.) The substance was reduced with phosphorus and hydriodic acid, when thioxanthene was obtained.



This substance was prepared from *o*-thiolbenzoic acid and toluene in concentrated sulphuric acid, the minor details of the process being the same as those already described. When crystallised from hot acetone, the substance appears to retain some impurity of lower carbon content; it was therefore further purified by distillation, which may be conducted under the ordinary pressure with small quantities without decomposition. *Methylthioxanthone* was obtained in this way as a pale yellow, crystalline solid, which melted at 66–67°. It is very soluble in most organic media, sparingly in ether, and insoluble in water. It sublimes slowly when heated to about 150°, and is then obtained in very pale yellow needles:

0.1072 gave 0.2900  $\text{CO}_2$  and 0.0424  $\text{H}_2\text{O}$ .  $\text{C}=73.8$ ;  $\text{H}=4.39$ .

$\text{C}_{14}\text{H}_{10}\text{OS}$  requires  $\text{C}=74.3$ ;  $\text{H}=4.43$  per cent.



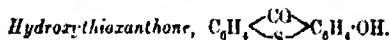
The preparation from anisole and *o*-thiolbenzoic acid was conducted in the usual manner. The product was crystallised from chloroform, and was obtained in bright yellow needles, which melted at 129°. It is soluble in most organic media, the solution in glacial acetic acid showing a strong violet fluorescence. The yield was about 80 per cent. of the theoretical:

0.2014 gave 0.5107  $\text{CO}_2$  and 0.0823  $\text{H}_2\text{O}$ .  $\text{C}=69.16$ ;  $\text{H}=4.5$ .

0.2450 „ 0.2447  $\text{BaSO}_4$ .  $\text{S}=13.7$ .

0.2076 „ 0.1589  $\text{AgI}$ .  $\text{OMe}=12.0$ .

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}$  requires  $\text{C}=69.4$ ;  $\text{H}=4.1$ ;  $\text{S}=13.3$ ;  $\text{OMe}=12.8$  per cent.



This was prepared from phenol and *o*-thiolbenzoic acid as usual. The precipitate obtained by pouring the acid solution into water was collected, and, after being washed with water, was dissolved in aqueous sodium hydroxide. This solution of the sodium salt was saturated with carbon dioxide, when the phenol was liberated as a yellow, crystalline powder. It was collected, dried, and then extracted with chloroform. The solvent was evaporated, and the residue crystallised from moist acetone. Two different samples of the crystals were analysed:

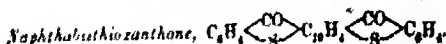
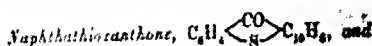
0.1852 gave 0.4520  $\text{CO}_2$  and 0.0534  $\text{H}_2\text{O}$ .  $\text{C}=65.1$ ;  $\text{H}=3.2$ .

0.1338 „ 0.3175  $\text{CO}_2$  „ 0.0448  $\text{H}_2\text{O}$ .  $\text{C}=64.7$ ;  $\text{H}=3.7$ .

$\text{C}_{13}\text{H}_8\text{O}_2\text{S}$  requires  $\text{C}=65.27$ ;  $\text{H}=3.7$  per cent.



It will be observed that the content of carbon is somewhat low for the anhydrous compound, but this seems not to be due to impurity, since the samples analysed were from successive fractions of the crystallisation. Hence it may be assumed that the substance contains water of crystallisation, and this behaviour has been observed with some of the polyhydroxyxanthones. However, attempts to remove water by heating to  $100^{\circ}$  were unsuccessful. *Hydroxythioxanthone* forms bright yellow prisms, which are readily soluble in most organic media and in aqueous sodium hydroxide, giving orange solutions of the sodium salt; it melts at  $214-215^{\circ}$ .



The preparation was conducted in the usual manner. The precipitate obtained on pouring the acid solution into water was apparently colloidal, and it was therefore isolated by removing the mother liquor with a Fikell's filter. The removal of carboxylic acids in the form of sodium salts and the final washing with water was effected by the same means. The yellow mass was then treated with a current of steam to remove excess of naphthalene, and, after being dried, it was repeatedly extracted with much acetone. On cooling the solution, the bithioxanthone separated almost completely in microscopic prisms, these were recrystallised for analysis:

0.1087 gave 0.2898  $\text{CO}_2$  and 0.0309  $\text{H}_2\text{O}$ .  $\text{C} = 72.69$ ;  $\text{H} = 3.38$ .

0.1084 " 0.2872  $\text{CO}_2$  " 0.0296  $\text{H}_2\text{O}$ .  $\text{C} = 72.24$ ;  $\text{H} = 3.03$ .

$C_{20}H_{12}O_2S_2$  requires  $\text{C} = 72.72$ ;  $\text{H} = 3.03$  per cent.

*Naphthalbithioxanthone* is almost insoluble in cold organic media, and it does not melt below  $280^{\circ}$ . The acetone mother liquor from the bithioxanthone was evaporated and allowed to cool, when a further small quantity of that substance separated. The filtrates from this were completely evaporated, and the residue recrystallised from acetone. *Naphthothioxanthone* was thus obtained in yellow prisms, which melt at  $186^{\circ}$ . It is soluble in sulphuric acid, giving a green fluorescence:

0.1271 gave 0.3643  $\text{CO}_2$  and 0.0364  $\text{H}_2\text{O}$ .  $\text{C} = 78.2$ ;  $\text{H} = 3.2$ .

0.276 in 20.0 of naphthalene, gave  $\Delta t = -0.380^{\circ}$ .  $\text{M.W.} = 262$ .

$C_{17}H_{10}OS$  requires  $\text{C} = 77.9$ ;  $\text{H} = 3.8$  per cent.  $\text{M.W.} = 255$ .



This was prepared as usual from  $\beta$ -naphthylamine and *o*-thiolbenzoic acid. The product was crystallised from hot chloroform, from which it separated in mustard-yellow prisms:

0.1613 gave 0.4333  $CO_2$  and 0.0530  $H_2O$ .  $C=73.35$ ;  $H=3.65$ .

0.2929 " 0.2445  $BaSO_4$ .  $S=11.5$ .

$C_{17}H_{11}ONS$  requires  $C=73.65$ ;  $H=3.96$ ;  $S=11.65$  per cent.

$\beta$ -Aminonaphthalenthione melts at  $213^\circ$ . The pale buff-coloured *platinichloride* is insoluble in cold water. The yield of this derivative was good, 5 grams of the pure product being obtained from 5 grams of *o*-thiolbenzoic acid and excess of  $\beta$ -naphthylamine. A small quantity of the corresponding bithioanthone was formed, but it was not more closely examined.

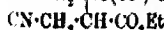
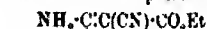
In conclusion we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the cost of these experiments.

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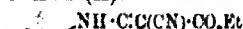
### CXVIII.—The Formation and Reactions of Imino-compounds. Part XIII. The Constitution of Ethyl $\beta$ -Imino- $\alpha$ -cyanoglutarate and of its Alkyl Derivatives.

By ARTHUR FRED CAMPBELL and JOCELYN FIELD THORPE.

In Part X of this series (Trans., 1909, 95, 1506) an instance was recorded, in which the five-membered ring, containing four carbon atoms and one nitrogen atom, was readily formed by the action of ethyl ethoxide, or of a sodium compound dissociating in solution, on a  $\gamma$ -amino-nitrile. Thus the open-chain compound represented by formula (I) could not be isolated from the product of the interaction of iodoacetoneitrile and the sodium compound of ethyl  $\beta$ -amino- $\alpha$ -cyanoglutarate, the only substance formed being the pyrrole derivative represented by formula (II):



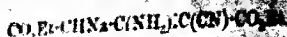
(I.)



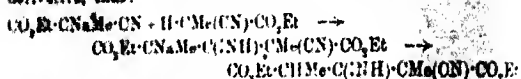
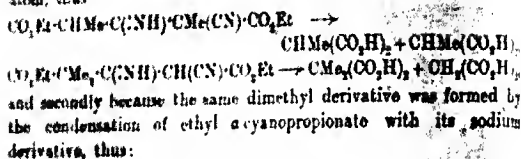
(II.)

It was also shown that ethyl  $\gamma$ -imino- $\alpha$ -cyanoglutarate reacts

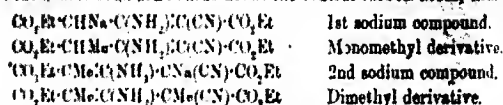
entirely as an amino-compound, and that the sodium compound formed from it by the action of alcoholic sodium ethoxide has the constitution:



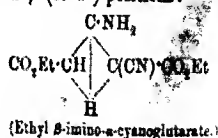
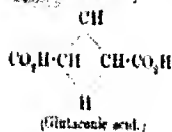
In Part I of this series (Trans., 1904, 86, 1787), in which the alkylation of ethyl  $\beta$ -amino- $\alpha$ -cyanoglutarate was described, it was stated that the introduction of the second methyl group into the molecule led to the displacement of the hydrogen atom attached to the cyanoacetic residue, and not of the remaining hydrogen atom of the methylene group. The proof of this statement was obtained in two ways, first because the dimethyl derivative on complete alkaline hydrolysis gave only methylmalonic acid, and not a mixture of dimethylmalonic and malonic acids, which would have been the case had the two methyl groups been attached to the same carbon atom, thus:



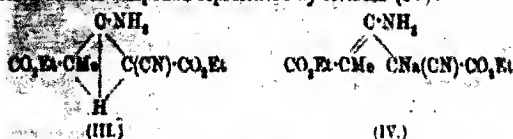
Since that time, however, it has been ascertained that compounds of this type are true amino-compounds which exhibit no chemical evidence of reacting in an imino-form, and hence it follows that before the methyl group can enter the cyanoacetic residue a shifting of the double bond must ensue about the central carbon atom, thus:



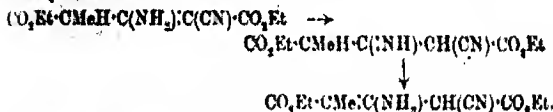
A change of this kind would suggest the presence of an alternating (mobile) hydrogen atom capable of passing between the  $\alpha$ - and  $\alpha'$ -carbon atoms similar to that which it was suggested might be present in the molecule of glutamic acid, and thus account for the identity of the  $\alpha$ - and  $\gamma$  (or  $\alpha'$ ) positions:



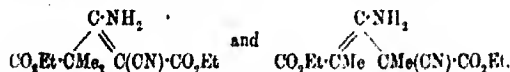
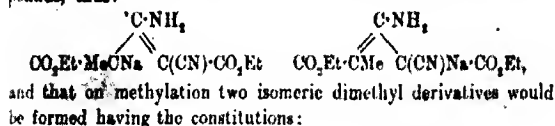
If this view is correct, the methylation of the amino-nitrile would lead to the formation of a monomethyl derivative represented by formula (III), which, on treatment with sodium ethoxide, would yield a sodium compound represented by formula (IV):



This view depends entirely on the assumption that the compound is a true amino-compound, because, if it can be shown that it possesses an imino-phase, the "wandering" of the double bond can be explained as follows:



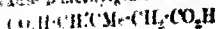
The experimental evidence on this point has, however, led us to the conclusion that a compound of the above type does not possess an imino-phase, but reacts only in the amino-form (Trans., 1909, 95, 1508). If this is so, and we adduce some further evidence on this point later, then it might be expected that the swing of the hydrogen atom would lead to the formation of two sodium compounds, thus:



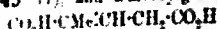
We have carefully repeated the work previously done, using larger quantities of material, which we have subjected to an exhaustive process of fractional recrystallisation, and have succeeded, not only in isolating the two isomeric dimethyl derivatives represented above, but have been able to obtain one of them (the *ac*-dimethyl derivative) in its stereoisomeric *cis*- and *trans*-forms.

The recently published work by Feist on the alkylglutaconic acids (*Annalen*, 1909, 370, 41), together with his previous paper on this subject (*Annalen*, 1906, 345, 77), shows that the explanation advanced by one of us (Trans., 1905, 87, 1669) to account for the fact that glutaconic acid and several of its derivatives cannot be

obtained in *cis* and *trans* forms corresponding with maleic and fumaric acid does not apply to the monoalkyl derivatives of glutamic acid, because  $\beta$ -methylglutamic acid,



(*Annalen*, 1906, 345, 77), and  $\alpha$ -methylglutamic acid,



(*Annalen*, 1907, 370, 4), can be isolated in *cis*- and *trans*-forms.

Still, as we explained some time ago (*Proc.*, 1906, 22, 146), this does not necessarily show that our suggestion as to the constitution of glutamic acid is wrong, because it is quite conceivable that the entering of a methyl group may so affect the mobility of the hydrogen atom owing to steric conditions or otherwise, as to bring about the fixing of the double bond, and hence lead to the conditions which allow the *cis*- and *trans*-forms to exist.

Until it can be shown that glutamic acid can be isolated in *cis*- and *trans*-modifications, we maintain that our explanation of the constitution of this acid is the one most in accordance with the experimental facts.

Apart, however, from any considerations of this kind, it is certain that whenever the conditions arise in the molecule of the alkyl glutaric acids which, according to our view, causes the certain fixation of the double bond, then the phenomenon of stereoisomerism always occurs, and the *cis*- and *trans*-forms can be isolated without difficulty. This is always the case in derivatives of glutaric acid when the two  $\alpha$ -hydrogen atoms are substituted, thus:  $\text{CO}_2\text{H}\cdot\text{CR}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , and, therefore, in the analogous case of ethyl  $\beta$ -amino  $\alpha$ -cyanoglutarate, should also occur when the corresponding hydrogen atoms are displaced, as is the case in both the  $\alpha\alpha$ - and  $\alpha\alpha'$ -dimethyl derivatives, thus:

$\alpha\alpha'$ -Dimethyl derivative,  $\text{CO}_2\text{Et}\cdot\text{CMc}\cdot\text{C}(\text{NH}_2)\cdot\text{CMc}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

$\alpha\alpha$ -Dimethyl derivative,  $\text{CO}_2\text{Et}\cdot\text{CMc}_2\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

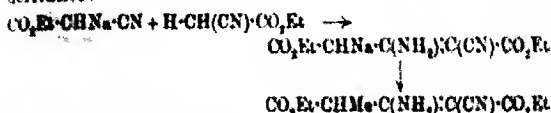
The great difficulty entailed by separating five different substances by fractional recrystallisation has prevented us up to the present from being able to isolate the two forms of the  $\alpha\alpha'$ -dimethyl derivative, but, as already mentioned, we have separated the *cis*- and *trans*-forms of the  $\alpha\alpha$ -dimethyl derivative, which are well defined crystalline substances, the constitutions of which are clearly shown by the products they yield on hydrolysis.

Before proceeding with the separation of these dimethyl derivatives, we decided, in the first instance, to investigate the monomethyl derivative,



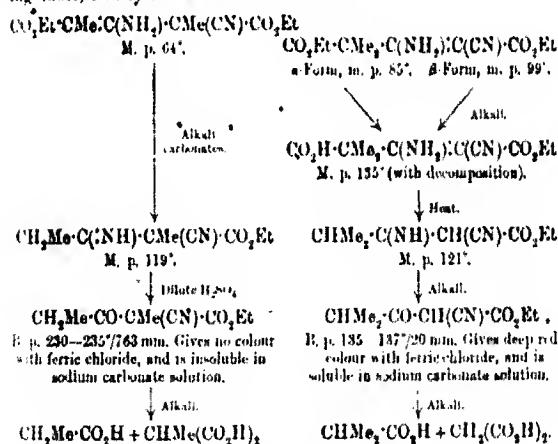
in order to ascertain whether it could be isolated in *cis*- and *trans*-modifications.

With this object in view, we prepared large quantities of this compound, both by the direct methylation of the sodium compound formed in the condensation of ethyl cyanoacetate and its sodium derivative:



and by the alkylation of pure ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate by means of sodium ethoxide and methyl iodide. The product in each case was found to be a pure homogeneous compound, which, although subjected to repeated fractional recrystallisation, failed to reveal the presence of any second substance.

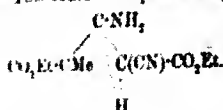
The methyl derivative was then further methylated in the usual manner, and from the portion soluble in benzene three substances were isolated by fractional recrystallisation from dilute alcohol, and finally obtained pure. Their behaviour, as indicated in the following table, clearly indicated their structure:



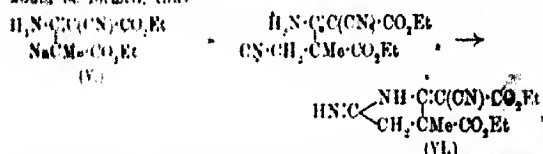
The terms  $\alpha$ - and  $\beta$ -forms are used because it was not found possible to decide between the *cis*- and *trans*-modifications.

It is evident therefore that the second methyl group unites with both the  $\alpha$ - and  $\alpha'$ -carbon atoms of ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate, although we find that the amount of the  $\alpha\alpha'$ -dimethyl derivative formed is very much less than that of the  $\alpha\alpha'$ -dimethyl derivative. These facts are in accordance with the assumption that the hydrogen atom of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate alternates between

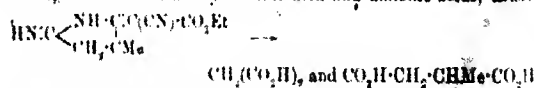
the  $\alpha$  and  $\alpha'$  carbon atoms as in glutamic acid, but that the period of time during which the hydrogen atom is attached to the  $\alpha'$  carbon atom is greater than that during which it is attached to the  $\alpha$  carbon atom. This could be represented graphically thus:



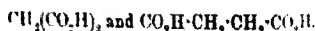
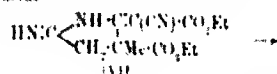
So far as could be judged from the quantity of the  $\alpha,\alpha$ -dimethyl derivative formed in the above methylation, the amount was not more than 15 per cent. of the total product, and it is evident therefore that the phase during which the hydrogen atom swings towards the  $\alpha$  carbon atom is very short. In order therefore to settle this point with greater certainty, we decided to treat the sodium compound of ethyl  $\beta$  imino  $\alpha'$  cyano  $\alpha$  methylglutarate with ethyl acetoneitrile, because, whether the sodium atom acted on the  $\alpha$  or  $\alpha'$  carbon atom, a pyrrole derivative would be formed, which could easily be isolated and identified. The formation of pyrrole derivatives in this manner has been already described (Trans., 1909, 95, 1506), and, therefore, if, in the above condensation, the sodium acted on the  $\alpha$  carbon atom (V) a pyrrole derivative (VI) would be formed, thus



and this compound would undergo disruption with strong alkalis, yielding a mixture of methylsuccinic acid and malonic acids, thus:

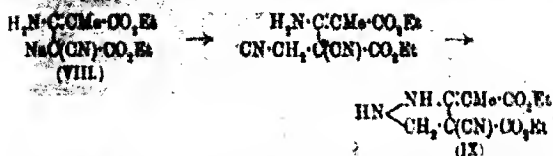


in the same manner as ethyl 2 imino-4-carbethoxytetrahydropyrrolidene-5-cyanacetate (VII) (Trans., 1909, 95, 1513), which yields under these conditions a mixture of succinic and malonic acids:

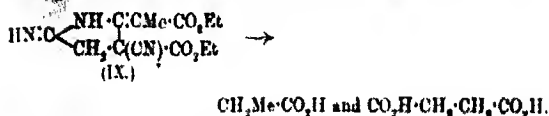


On the other hand, if the sodium atom attached itself to the cyanoacetic residue as in formula (VIII), the action of iodoaceto-

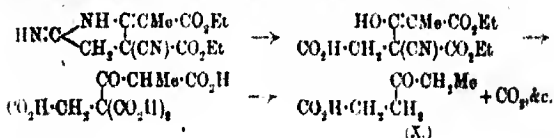
nitrile would produce a pyrrole derivative corresponding with formula (IX):



It is difficult to predict the manner in which this pyrrole derivative would undergo disruption on alkaline hydrolysis, but if it behaved in the same manner as ethyl 2-imino-4-carbethoxytetrahydropyrrolidene-5-cyanoacetate, it would yield succinic acid (or ethanetricarboxylic acid) and propionic acid, thus:



But as a matter of fact the pyrrole derivative which is formed by the action of iodoacetone on the sodium compound of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate undergoes disruption in another manner, which, however, clearly shows that it possesses a constitution represented by formula (IX), for the product consists of homolevulinic acid (X), carbon dioxide, and ammonia. The disruption has therefore taken place in the following way:

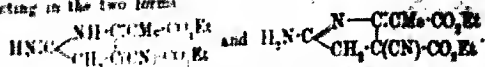


The formation of the compound of formula (IX), which we have called *ethyl 2-imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5- $\alpha$ -propionate*, is therefore not only another instance of the formation of the pyrrole ring from a  $\gamma$ -amino-nitrile, but its formation also supplies clear proof of the predominant position of the second sodium atom entering the molecule of ethyl  $\beta$ -imino- $\alpha$ -cyano-glutarate. We were quite unable to detect the presence of the pyrrole derivative corresponding with formula (VI), and, in the condensation, the whole of the amino-ester not condensed to form the above-mentioned pyrrole derivative of formula (IX) was recovered unchanged.

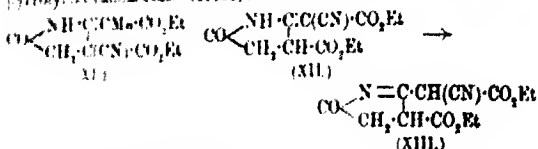
Ethyl 2-imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5- $\alpha$ -pro-



pyrrole is a tautomeric amino-imino (ketimino-enamic) compound reacting in the two forms

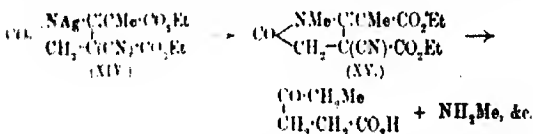


It melts at  $210^\circ$  and is converted either by hydrochloric acid or by nitrous acid into ethyl 4-cyano-2-keto-4-carbethoxytetrahydropyrrolidene-5-carboxylate (XI). This ketone is instantly soluble in sodium carbonate solution, and is therefore the pyrrole form as represented above. This form is, moreover, stable, and does not appear to pass over to the copyrrole form corresponding with the transformation of ethyl 2-keto-4-carbethoxytetrahydropyrrolidene-5-cyanocarboxylate (XII) into ethyl 2-keto-4-carbethoxydihydroisopyrrolyl-5-cyanocarboxylate (XIII).

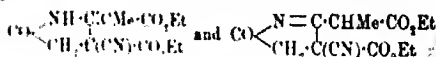


(compare Traus, 1909, 95, 1512).

It forms salts with alkalis, having the metal attached to the nitrogen atom, when the silver salt (XIV) is treated with methyl iodide, an *N*-methyl derivative (XV) is formed, the constitution of which is proved by the formation of homolactic acid, methylamine, and ammonia from it on alkaline hydrolysis:



It is evident therefore that the desmotropism of the pyrrole and copyrrole forms of these compounds is determined by the cyanoacetic residue outside the pyrrole ring, and that it ceases when a less negative group is in this position. Whether or not the two forms



are tautomeric, we have at present no means of ascertaining, although it is highly probable that they are so.

Our conclusions are therefore as follows.

(1) That ethyl  $\beta$ -amino- $\alpha$ -cyanoglutarate is constituted in an analogous manner to glutamic acid, that is to say, there is tautomerism between the  $\alpha$  and  $\alpha'$  carbon atoms.

(2) That the first hydrogen displaced by sodium on treating this substance with sodium ethoxide is not the mobile hydrogen atom producing tautomerism, but the remaining hydrogen atom attached to the  $\alpha$ -carbon atom.

(3) That when this hydrogen atom is replaced the tautomeric nature of the compound becomes evident, because the next sodium atom unites with either the  $\alpha$ - or  $\alpha'$ -carbon atom.

(4) That so long as the mobile hydrogen atom remains, stereoisomerism forms cannot be isolated, but so soon as the double bond is fixed by the entrance of two methyl groups, the compound can exist in *cis*- and *trans*-forms.

#### EXPERIMENTAL

##### *Ethyl $\beta$ -Imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate,* $\text{CO}_2\text{Et}\cdot\text{CHMe}\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ .

The preparation of this substance in large quantities was effected in two different ways in order to see whether by varying the method of production any difference in the composition of the product could be detected.

(1) *From the sodium compound formed in the condensation of ethyl cyanoacetate with its sodium derivative, by treatment with methyl iodide.*—This is by far the best method for obtaining large quantities of the pure methyl derivative, and as the process was used for the production of the methyl derivative employed in this research and differed from that previously given (Trans., 1904, 85, 1747), it is advisable to give the full experimental details. 11.5 Grams of sodium were dissolved in 150 grams of alcohol, the solution was mixed with 113 grams of ethyl cyanoacetate, and then heated on the water-bath for two hours. At the end of this time the clear, brownish-coloured solution was cooled and mixed with 75 grams of methyl iodide, the solution being heated on the water-bath for a further two hours. Water was then added, and the product distilled in a current of steam until the distillate became free from oil. The residue in the flask, which solidified on cooling, was then collected by filtration.

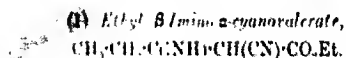
(2) *From Ethyl  $\beta$ -Imino- $\alpha$ -cyanoglutarate by treatment with sodium ethoxide and methyl iodide.*—The process adopted in this case was essentially the same as above, pure ethyl  $\beta$ -imino- $\alpha$ -cyanoglutarate, prepared as already described (Trans., 1909, 95, 1518), being treated in alcoholic solution with an equivalent amount of sodium dissolved in alcohol, and then with a slight excess of methyl iodide, the reaction being completed by heating on the water-bath for two hours. The product was purified and isolated by steam distillation in the manner described above.

The solid product prepared by each of these methods was then separately subjected to a process of fractional recrystallisation from dilute alcohol. The melting point of each fraction was 63–64°, the melting point previously found for ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylglutarate, and allowing for a small quantity of oily product which could not be obtained crystalline, it can be stated with certainty that no other compound is formed in these reactions.

As the method of fractional recrystallisation from dilute alcohol in this case was the same as that adopted with the dimethyl derivatives described below, the opportunity may be taken of briefly describing it. In every case the solid substance was dissolved in warm alcohol, and after the solution had been cooled, sufficient water was added until it became cloudy, when a drop of alcohol again produced a clear solution, which was allowed to remain. In the course of a few hours, crystals had separated, which were collected. Water was then added to the mother liquor until it was again cloudy, when alcohol was added until clear, and a fresh crop of crystals obtained by keeping the solution for some time. This process was repeated until the mother liquor ceased to give a precipitate of oil on the addition of water. In this way several fractions were obtained, which were each subjected to the same process, the fractions being combined and recrystallised together so soon as they showed the same melting point.

*The Methylation of Ethyl  $\beta$ -Imino- $\alpha$ -cyano- $\alpha$ -methylglutarate.*

As it was found that by the complete methylation of ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylglutarate under the condition employed only one methyl group could be introduced, the methylation of this compound to form the dimethyl derivative was effected by means of excess of sodium ethoxide and methyl iodide, the operation being carried out twice. This was found to be necessary, because, when the compound was methylated once only, some unchanged mono-methyl derivative was always found in the product.



This substance is always formed in the above methylation, owing to the elimination of a carbethoxy-group from ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylglutarate by the action of sodium ethoxide. It appeared to be impossible to prevent this action even by keeping the temperature very low. The method adopted to effect methylation was as follows. Twenty-four grams of ethyl  $\beta$ -imino- $\alpha$ -cyano- $\alpha$ -methylglutarate were mixed with a solution of 3 grams

of sodium dissolved in 50 grams of alcohol, and 16 grams of methyl iodide added. After the solution had been heated on the water-bath until a test portion showed a neutral reaction on dilution, water was added, and the oil extracted with ether. The residue left on evaporating the ether was then again treated with 3 grams of sodium dissolved in alcohol and 16 grams of methyl iodide in the same manner as above, when the ultimate product, which became solid, was spread on a porous plate until free from oil.

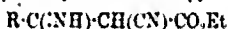
The solid residue was then rubbed with cold benzene, in which the greater portion dissolved, leaving a crystalline substance, which, after being twice recrystallised from benzene, yielded fern-shaped crystals, melting at  $121^{\circ}$ :

0.2021 gave 0.4254  $\text{CO}_2$  and 0.1295  $\text{H}_2\text{O}$ .  $\text{C} = 57.41$ ;  $\text{H} = 7.12$ .

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_2$  requires  $\text{C} = 57.1$ ;  $\text{H} = 7.1$  per cent.

The analytical data and the formation of ethyl  $\alpha$ -cyano- $\beta$ -keto valerate,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}$  (Found,  $\text{C} = 56.88$ ;  $\text{H} = 6.45$ . Calc.,  $\text{C} = 56.8$ ;  $\text{H} = 6.5$  per cent.), from this substance, on treatment with dilute potassium hydroxide, showed it to be ethyl  $\beta$ -imino- $\alpha$ -cyanovalerate.

It may be mentioned here that by far the best method for transforming an imino-compound of the type



into the corresponding ketone is by warming it with aqueous potassium hydroxide solution until all has dissolved, and then acidifying the clear solution in order to precipitate the ketone. These compounds are tautomeric ketimino-enamic derivatives having a longer enamic than ketimino-phase. They are consequently only slowly hydrolysed by acids, whereas with alkalis they are rapidly transformed into the alkali salt,  $\text{R}\cdot\text{C}(\text{OK})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ , which is very stable towards boiling alkalis.

(2) *The  $\alpha$ - and  $\beta$ -forms of Ethyl  $\beta$ -Imino- $\alpha'$ -cyano- $\alpha\alpha$ -dimethyl-glutarate,  $\text{CO}_2\text{Et}\cdot\text{CMe}_2\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$ .*

The benzene solution obtained in the above separation was evaporated to dryness, and the residue again triturated with cold benzene, when a further small quantity of the substance melting at  $121^{\circ}$  was obtained. The solid residue, after again evaporating the benzene, was then fractionally recrystallised from dilute alcohol in the manner already described. The first fractions indicated the presence of some substance much less soluble in the solvent than the other constituents of the mixture. This was therefore collected, and finally obtained pure by recrystallisation from absolute alcohol,

from which solvent it separated in long, silky needles, melting at  $79^{\circ}$ .

0.1937 gave 0.4027  $\text{CO}_2$  and 0.1254  $\text{H}_2\text{O}$ .  $\text{C}=56.70$ ;  $\text{H}=7.20$ .

$\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_2$  requires  $\text{C}=56.70$ ;  $\text{H}=7.1$  per cent.

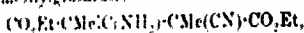
The above is a form of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha\alpha$ -dimethylglutarate is so much less soluble in dilute alcohol than the other substances present in the mixture that its separation is a comparatively simple matter.

The residues from which the substance melting at  $99^{\circ}$  had been, so far as possible separated, were then subjected to a further process of fractional recrystallisation, and ultimately two more compounds were isolated in a pure condition. The first of these, which was found to be present in large quantities, separated from dilute methyl alcohol in small prisms, melting at  $64^{\circ}$ :

0.1790 gave 0.3710  $\text{CO}_2$  and 0.1167  $\text{H}_2\text{O}$ .  $\text{C}=58.42$ ;  $\text{H}=7.25$ .

$\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_2$  requires  $\text{C}=56.70$ ;  $\text{H}=7.1$  per cent.

Since this compound showed all the reactions of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha\alpha$ -dimethylglutarate:



already described (Trans., 1904, 85, 1751), its constitution is evidently represented by this formula. The second substance, which was present in small amount, was obtained from the mother liquors after the substance melting at  $64^{\circ}$  had been, so far as possible, separated. It was ultimately obtained from dilute methyl alcohol in large, rectangular prisms, melting at  $85^{\circ}$ :

0.1462 gave 0.3925  $\text{CO}_2$  and 0.1209  $\text{H}_2\text{O}$ .  $\text{C}=57.51$ ;  $\text{H}=7.25$ .

$\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}_2$  requires  $\text{C}=56.70$ ;  $\text{H}=7.1$  per cent.

The reactions of this compound, given below, showed that it had the same structural formula as that of the compound melting at  $79^{\circ}$ . It was therefore recrystallised several times in order to ascertain whether it was an impure form of this compound. Recrystallisation, however, failed to alter the melting point, and this fact, together with the well defined crystalline form, which is quite different from that of the compound melting at  $99^{\circ}$ , showed conclusively that it was a homogeneous substance stereoisomeric with the compound of higher melting point.

The mother liquors yielded further crystalline crops on further dilution, but these possessed indefinite melting points, and by repeated fractional recrystallisation yielded further small quantities of the compounds already described. The ultimate fractions separated as oils, which could not be induced to solidify, and it was not found possible to isolate any crystalline substance from them.

*The Products of Hydrolysis of the  $\alpha$ - and  $\beta$ -forms of Ethyl  $\beta$ -Imino- $\alpha'$ -cyano- $\alpha$ -dimethylglutarate.*

(1) *Ethyl Hydrogen  $\beta$ -Imino- $\alpha'$ -cyano- $\alpha$ -dimethylglutarate,*  
 $\text{CO}_2\text{H}\cdot\text{CMe}_2\cdot\text{C}(\text{NH}_2)\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}.$

Both the  $\alpha$ - and  $\beta$ -forms of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -dimethylglutarate yield this hydrogen salt on treatment with potassium hydroxide solution, the conditions found most suitable being as follows. Five grams of the imino-compound were added to a solution of one and a-half times the calculated quantity of potassium hydroxide dissolved in methyl alcohol, and the solution, which became warm, allowed to remain until a test portion gave a clear solution on the addition of water, when the excess of methyl alcohol was evaporated so far as possible under diminished pressure, and dilute hydrochloric acid added to the residue until it gave an acid reaction. The oil, which was precipitated on the addition of the acid, solidified on scratching, and when recrystallised from dilute alcohol yielded small prisms melting at  $135^\circ$  with vigorous evolution of carbon dioxide:

0.1910 gave 0.3712  $\text{CO}_2$  and 0.1083  $\text{H}_2\text{O}$ .  $\text{C} = 53.00$ ;  $\text{H} = 6.30$ .

$\text{C}_{10}\text{H}_{14}\text{O}_4\text{N}_2$  requires  $\text{C} = 53.1$ ;  $\text{H} = 6.2$  per cent.

The hydrogen salt can also be recrystallised from water, but care must be taken not to boil the solution, otherwise some carbon dioxide is evolved.

(2) *Ethyl  $\beta$ -Imino- $\alpha$ -cyanoisobutylacetate,*  
 $\text{C}_5\text{H}_7\cdot\text{C}(\text{CN})\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$

This substance is formed by heating the hydrogen ethyl salt described above at  $150^\circ$  until the evolution of carbon dioxide has ceased. For this purpose the salt was placed in a test-tube and heated in a bath of sulphuric acid at the requisite temperature, and as soon as the evolution of gas had ceased, it was cooled, and the solid which then formed was purified by spreading on a porous plate. When recrystallised from dilute alcohol, it formed glistening plates, melting at  $121^\circ$ :

0.1873 gave 0.4063  $\text{CO}_2$  and 0.1315  $\text{H}_2\text{O}$ .  $\text{C} = 59.16$ ;  $\text{H} = 7.80$ .

$\text{C}_9\text{H}_{11}\text{O}_4\text{N}_2$  requires  $\text{C} = 59.3$ ;  $\text{H} = 7.7$  per cent.

(3) *Ethyl Cyanoisobutylacetate,  $\text{C}_5\text{H}_7\cdot\text{CO}\cdot\text{CH}(\text{CN})\cdot\text{CO}_2\text{Et}.$*

In order to prepare this substance from the above imino-compound, it is necessary to warm it gently with an aqueous

solution containing slightly more than the requisite quantity of potassium hydroxide to form the potassium salt,



The complete transformation of the imino-compound into the potassium salt is effected when the whole of the imino-compound has passed into solution, but care must be taken to keep the temperature as low as possible. When the clear alkaline solution is acidified, an oil is precipitated, which, when extracted by ether, yields a clear, mobile liquid boiling, on distillation, at 136–137°/20 mm.

0.2117 gave 0.1705 CO<sub>2</sub> and 0.1375 H<sub>2</sub>O. C=58.80; H=7.21.

C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>N requires C=59.0; H=7.1 per cent.

The ketone dissolves in aqueous sodium carbonate with effervescence, and gives in alcoholic solution a deep red colour with ferric chloride.

The silver salt, C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>NAg, is precipitated as a white, micro-crystalline powder on adding the calculated quantity of silver nitrate solution to a neutral solution of the ammonium salt:

0.2612 gave 0.0934 Ag. Ag=37.17.

C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>NAg requires Ag=37.24 per cent.

(4) *Isobutyric Acid and Malonic Acid*.—These acids form the ultimate products of the hydrolysis of ethyl cyanoisobutyrylacetate, and can be isolated in the following way. The ketone is dissolved in excess of aqueous potassium hydroxide, and the solution boiled until ammonia ceases to be evolved, when it is acidified with dilute sulphuric acid and distilled in a current of steam until the distillate is no longer acid. The steam distillate is then rendered alkaline with ammonia, and evaporated on the water-bath to a small bulk. Silver nitrate solution is then added, and the precipitated silver salt recrystallised from hot water. (Found, Ag=55.21. Calc., Ag=55.34 per cent.) The acid was characterised as isobutyric acid by the formation of the calcium salt.

The residue from the steam distillation was then rendered alkaline and evaporated to dryness, the residue being acidified with hydrochloric acid and again evaporated. On extracting the solid residue in a Soxhlet apparatus with ether, a solid residue was obtained, which, when purified, melted at 132°, and was proved to be malonic acid. (Found, C=34.42; H=3.8. Calc., C=34.6; H=3.8 per cent.)

When ethyl β-amino-α'-cyano-α-dimethylglutarate in either its α or β form is boiled with excess of potassium hydroxide until all ammonia has been evolved, the product is found to consist of isobutyric acid, dimethylmalonic acid, and malonic acid. The first named can be isolated by distilling the acidified product of

hydrolysis in a current of steam in the manner already described, and the two last, which are extracted by ether from the evaporated residue, can be separated by taking advantage of the fact that dimethylmalonic acid is quite insoluble in cold concentrated hydrochloric acid, whereas malonic acid readily dissolves.

The above experiments were carried out with both the  $\alpha$ - and  $\beta$ -forms of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate, and there can therefore be no doubt as to these two compounds being stereoisomeric. The conditions under which one form is converted into the other could not be determined.

*The Formation of Pyrrole Derivatives from Ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate.*

*Ethyl 2-Imino-4-cyano-4-carbethoxytetrahydropyrrolidene-5- $\alpha$ -propionate,  $\text{HN} \cdot \text{C} \begin{cases} \text{NH} \cdot \text{C}(\text{Me})\text{CO}_2\text{Et} \\ \text{CH}_2 \cdot \text{C}(\text{CN})\text{CO}_2\text{Et} \end{cases}$*

This compound is formed by the action of iodoacetoneitrile on the sodium compound of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate under the following conditions. 2.3 Grams of sodium are dissolved in 50 grams of alcohol, and the solution is mixed with 24 grams of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate dissolved in as little alcohol as possible. 16.7 Grams of iodoacetoneitrile are then added to the cooled solution, and the mixture is heated on the water-bath for ten minutes. After this time the clear solution is poured into water, and the solution extracted by ether, when a crystalline substance remains undissolved and can be isolated by filtration. The ethereal solution deposits more of the substance after some time. The pyrrole derivative obtained in this way crystallises from alcohol in yellow plates, melting at  $216^\circ$ :

0.1810 gave 0.3715  $\text{CO}_2$  and 0.1070  $\text{H}_2\text{O}$ .  $\text{C} = 56.03$ ;  $\text{H} = 6.3$ .

$\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}_2$  requires  $\text{C} = 55.9$ ;  $\text{H} = 6.1$  per cent.

The yield of the pyrrole derivatives is very small, being only about 10 per cent. of the theoretical amount, the remainder of the ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate used in the experiment being recovered unchanged on evaporating the ethereal solution after all pyrrole derivative has crystallised out. It is evident, therefore, that under the experimental conditions employed, the major portion of the sodium compound of ethyl  $\beta$ -imino- $\alpha'$ -cyano- $\alpha$ -methylglutarate dissociates in the alcoholic solution, and reacts with iodoacetoneitrile as sodium ethoxide. No trace of any other pyrrole derivative could be isolated.

The compound melting at  $216^\circ$  is insoluble in cold aqueous sodium carbonate, but slowly passes into solution on boiling,



ammonia being evolved. If the solution is acidified after all ammonia has been given off the ketone, melting at  $128^{\circ}$  (see below), is precipitated. It dissolves in cold aqueous potassium hydroxide, forming a solution from which acetic acid precipitates it unchanged. It also dissolves in concentrated hydrochloric acid, forming a clear solution, from which the imino compound is precipitated by the addition of much water. The compound may be recrystallised from water.

*Ethyl 10-oxo-2-keto-3-carbethoxytetrahydropyrrolidene-5- $\alpha$ -propanoate*,  $\text{CO} \begin{array}{l} \text{NH} \cdot \text{C}(\text{Me}) \cdot \text{CO}_2\text{Et} \\ \text{CH}_2 \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et} \end{array}$

When a solution of the imino compound, melting at  $216^{\circ}$ , in concentrated hydrochloric acid is poured into an equal volume of boiling water a clear solution is obtained, from which, after the lapse of a few seconds, an oil suddenly separates. This oil solidifies when the solution is cooled and scratched, and the solid then obtained separates from dilute alcohol in small, colourless needles, melting at  $125^{\circ}$ .

0.1825 gave 0.3721  $\text{CO}_2$  and 0.0972  $\text{H}_2\text{O}$ .  $\text{C}=55.81$ ;  $\text{H}=5.81$ .

$\text{C}_{11}\text{H}_{15}\text{O}_5\text{N}_2$  requires  $\text{C}=55.7$ ;  $\text{H}=5.7$  per cent.

The ketone gives no colour with ferric chloride, and is soluble in aqueous sodium carbonate, yielding a clear solution, from which acids precipitate it unchanged. There is therefore no tendency for this substance to exhibit desmotropism.

The potassium salt,  $\text{CO} \begin{array}{l} \text{NK} \cdot \text{C}(\text{Me}) \cdot \text{CO}_2\text{Et} \\ \text{CH}_2 \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et} \end{array}$ , is precipitated as an oil when a solution of the ketone in dilute aqueous potassium hydroxide is mixed with excess of the reagent. The oil solidifies on keeping, and can be purified by recrystallisation from a small quantity of ethyl alcohol, from which it separates in small, colourless prisms. It is readily soluble in both ethyl and methyl alcohol.

0.2328 gave 0.0630  $\text{K}_2\text{SO}_4$ .  $\text{K}=12.13$ .

$\text{C}_{11}\text{H}_{13}\text{O}_5\text{N}_2\text{K}$  requires  $\text{K}=12.3$  per cent.

The silver salt,  $\text{CO} \begin{array}{l} \text{NAg} \cdot \text{C}(\text{Me}) \cdot \text{CO}_2\text{Et} \\ \text{CH}_2 \cdot \text{C}(\text{CN}) \cdot \text{CO}_2\text{Et} \end{array}$ , is formed as a gelatinous precipitate when the calculated quantity of silver nitrate solution is added to a solution of the potassium salt in water. It can be dried at  $80^{\circ}$  without undergoing change, and is then obtained as an amorphous powder, which is characterised by being instantly soluble in dry benzene.

0.2871 gave 0.0798  $\text{Ag}$ .  $\text{Ag}=27.79$ .

$\text{C}_{11}\text{H}_{11}\text{O}_5\text{N}_2\text{Ag}$  requires  $\text{Ag}=27.9$  per cent.

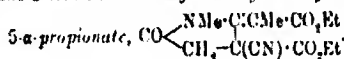
*Hydrolysis of the Ketone to Homolactic Acid.*

The hydrolysis of ethyl 4-cyano-2-keto-4-carbomethoxytetrahydropyrrolidene-5- $\alpha$ -propionate to homolactic acid is effected in the following manner. Five grams of the ketone are dissolved in excess of aqueous potassium hydroxide, and the solution is boiled until all ammonia has been evolved, when the solution is rendered strongly acid by means of hydrochloric acid, and the acidified solution again boiled until all carbon dioxide has been eliminated. It is then extracted with ether and the ethereal solution evaporated, when a syrup is obtained which distils at 183°/20 mm. as a viscid oil, and solidifies when cooled in a mixture of ice and salt. The solid melts at 32° (compare Zanetti, *Gazzetta*, 1891, **21**, ii, 169; Hillert, *Annalen*, 1892, **268**, 69). (Found, C = 55.27; H = 7.80. Calc., C = 55.4; H = 7.7 per cent.)

The semicarbazone separates as a crystalline precipitate when a solution of semicarbazide hydrochloride dissolved in sodium acetate solution is added to an aqueous solution of the ketonic acid. It crystallises from alcohol, in which it is only sparingly soluble, in small prisms, melting and decomposing at 176°:

0.1803 gave 0.2959 CO<sub>2</sub> and 0.1116 H<sub>2</sub>O. C = 44.7; H = 6.8.

C<sub>11</sub>H<sub>13</sub>O<sub>5</sub>N<sub>3</sub> requires C = 44.9; H = 6.9 per cent.

*Ethyl 4-Cyano-2-keto-4-carbomethoxy-1-methyltetrahydropyrrolidene*

The above *N*-methyl derivative is best prepared by the action of methyl iodide on the silver salt of the ketone in dry benzene solution. Five grams of the ketone melting at 128° are converted into the silver salt in the manner described on page 1314, and a solution of the dried salt in dry benzene is mixed with excess of methyl iodide. The reaction starts at the ordinary temperature, silver iodide separating as soon as methyl iodide is added, and is completed by warming for a short time on the water-bath. The benzene solution, after being freed from silver iodide by filtration, is then evaporated to dryness, and the oil which remains is allowed to crystallise. It was purified by recrystallisation from dilute methyl alcohol, from which solvent it separated in small plates, melting at 75°:

0.1912 gave 0.3998 CO<sub>2</sub> and 0.1062 H<sub>2</sub>O. C = 57.02; H = 6.17.

C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>N<sub>2</sub> requires C = 57.1; H = 6.1 per cent.

*Hydrolysis of the N-Methyl Derivative to Homoleucic Acid and Methylamine.*

The hydrolysis was effected by the action of aqueous potassium hydroxide in the following manner. Three grams of the *N*-methyl derivative were added to a solution containing one and a-half times the quantity of potassium hydroxide necessary for complete hydrolysis, and the mixture was boiled under conditions which allowed the methylamine formed to be collected (compare Trans. 1902, 95, 1530). The hydrolysis proceeded rapidly, and was finished at the end of half an hour. The residue in the flask was then acidified, boiled until free from carbon dioxide, and extracted with ether. The ethereal extract, on being evaporated, yielded a mass, which solidified on cooling, and melted at 32°. It yielded  $\alpha$ -methylazobenzene, melting and decomposing at 176°, and was therefore homoleucic acid. (Found, C=44.77; H=6.78. Calc. C=44.9, H=6.9 per cent.)

The hydrochloric acid solution into which the volatile products of the hydrolysis had been led was then evaporated to a small bulk, and the solution, after being mixed with excess of platinic chloride solution, diluted with an equal volume of alcohol. The yellow plates which then separated were collected, dried, and analysed. (Found, Pt=41.18. Calc., Pt 41.34 per cent.)

The base was therefore methylamine.

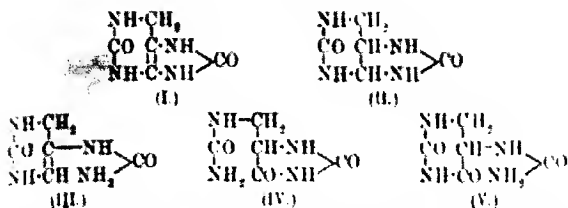
Much of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society and from the Research Fund of the Chemical Society, for which we desire to express our indebtedness.

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CXIX.—*A Synthesis of Tetrahydrouric Acid.*

By EDWARD PERCY FRANKLAND.

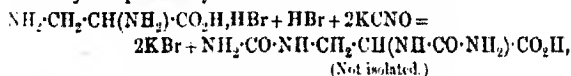
TAYLOR has shown (*Ber.*, 1901, 34, 258) that the electrolytic reduction of uric acid on a lead cathode leads to the formation of three different substances in proportions varying with the experimental conditions, namely, purone (II), isopurone (III), and tetrahydrouric acid (IV) or (V):



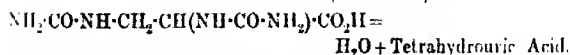
Desoxyuric acid itself (I), probably the first step in the reduction, could not be isolated, and Tafel considered that this substance either was at once reduced further to purone or that it reacted with the elements of water to form tetrahydouric acid, one of the rings opening in the process.

The present paper describes an attempt to synthesise this hypothetical desoxyuric acid, starting from  $\alpha\beta$ -diaminopropionic acid,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$ . The monohydrobromide of this amino-acid, together with the requisite quantity of either hydrobromic or hydrochloric acid for the saturation of the second amino-group, was allowed to react in aqueous solution with a corresponding weight (two molecules) of potassium cyanate.

The resulting urea derivative was in general not isolated owing to the difficulty experienced in its purification; it was dissolved in 25 per cent. hydrochloric acid, and the solution evaporated in order to form the corresponding hydantoin. This proved to be a beautifully crystalline substance, soluble in water, giving a solution having an acid reaction towards litmus, and melting with decomposition and gas evolution at  $216^\circ$ . The results of an analysis indicated clearly that this substance was the intermediate stage towards desoxyuric acid, namely, tetrahydouric acid, in which only one ring is closed with elimination of a molecule of water. The experiment thus resulted in the synthesis of tetrahydouric acid, although the method was not such as to enable a decision to be made between the two possible formulae (IV) and (V). These are based on Tafel's decomposition of tetrahydouric acid with baryta (*Ber.*, 1901, **34**, 1182) (which yielded one molecule of diaminopropionic acid and two molecules of carbon dioxide), and are confirmed by the present synthesis:



(Not isolated.)



A portion of the tetrahydouric acid thus obtained was dissolved in 25 per cent. hydrochloric acid, and the solution evaporated to a

# 1118 FRANKLAND, A SYNTHESIS OF TETRAHYDROURIC ACID.

syropy form which, by precipitating with alcohol, tetrahydrouric acid was recovered unchanged. Apparently the substance cannot be condensed to deoxyuric acid by this process.

The mother liquor from which the tetrahydrouric acid had been removed in the original preparation contained a syrupy substance, very soluble in water. This does not yield tetrahydrouric acid on further heating with hydrochloric acid, and it is possibly the hydantoin of a monourea derivative. Ellinger (*Ber.*, 1904, 37, 115) as well as Neuberg and Silbermann (*Ber.*, 1904, 37, 341) have shown that the diamino-group in diaminopropionic acid,  $\alpha$ -hydrochloride or hydrobromide is very resistant to the action of cyanic acid; a similar observation was made by Tafel and E. P. Frankland (*Ber.*, 1909, 42, 3134) in the case of the monohydrochloride of  $\beta$ -amino- $\alpha$ -methylaminopropionic acid, which yielded a mononitroso-derivative, the nitroso-group being presumably in the  $\alpha$ -position. It is suggested that in these cases the diamino-group may be shielded by internal salt formation with the carboxyl group. In the present instance it is possible that the amino acid reacts less readily with the second molecule of cyanic acid, and this would account for the smallness of the yield of tetrahydrouric acid. This view is strengthened by experiments made by the author on  $\alpha\beta$ -dibenzylaminopropionic acid in which case the reaction leads to the formation of a monourea-derivative only. This compound can be converted quantitatively into a hydantoin, leaving a free aminogroup, presumably in the  $\beta$ -position. The results of this work will be published in the near future.

## EXPERIMENTAL.

The diaminopropionic acid used in the following experiments was prepared by the action of concentrated ammonia solution on  $\alpha\beta$ -bromopropionic acid in sealed tubes at temperatures ranging from 80° to 120°.

The resulting hydrobromide,  $\text{NH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}\cdot\text{HBr}$ , was purified by recrystallisation from water, and melted and decomposed at 275° (uncorr.). Klebs (*Ber.*, 1893, 26, 2264; *Zeitsch. physiol. Chem.*, 1901, 21, 369), who was the first to isolate this salt, gave 275–276° as the decomposition point. (Found, Br=43.42.  $\text{C}_3\text{H}_8\text{N}_2\text{Br}$ , 44.24 per cent.)

2.4 Grams of the above hydrobromide were dissolved in warm water with the addition of 6.15 grams of a 45 per cent. solution of sodium bromide, and treated with an aqueous solution of 4 grams of potassium cyanate. Considerable effervescence followed the mixing of the solutions. The mixture was kept for about an hour, and was then concentrated slowly to a small bulk. When the

volume of the solution had been reduced to about 3 c.c., 10 grams of concentrated hydrochloric acid were added to the semicrystalline mass; the mixture was warmed for a few minutes, then allowed to cool, and the crystalline precipitate of potassium bromide collected by filtration and washed with concentrated hydrochloric acid. The filtrate and washings were concentrated to a syrupy mass on the water-bath, mixed with a little 25 per cent. hydrochloric acid, and evaporated almost to dryness on the water-bath. After boiling the residue with methyl alcohol, a further quantity of potassium bromide was filtered off; the total quantity obtained being 4.25 grams.

The methyl-alcoholic solution was evaporated nearly to dryness, and the residue dissolved with a small quantity of hot water. The solution was allowed to cool, and sown with crystals of tetrahydronic acid obtained from a previous experiment. After a few minutes a crystalline precipitate separated; it was collected, washed with a small quantity of cold water, with absolute alcohol, and finally with ether. The weight of tetrahydronic acid thus obtained was 0.58 gram. Another experiment, starting from 3.75 grams of the hydrobromide of diaminopropionic acid, yielded 1.25 grams of tetrahydronic acid. The substance melted at 215° with gas evolution to a colourless liquid, was readily soluble in hot water, the solution having an acid reaction to litmus, only very sparingly soluble in absolute ethyl alcohol, and crystallised anhydrous from water in acicular prisms and hexagonal, prismatic plates.

For the purposes of analysis a specimen of the substance obtained by this method was recrystallised twice from water, and it melted and decomposed at 216°. Tafel gives 212–213° as the melting point of tetrahydronic acid. (Found, C=34.57, 34.60; H=4.90, 4.84; N=32.53. Calc., C=34.85; H=4.65; N=32.56 per cent.)

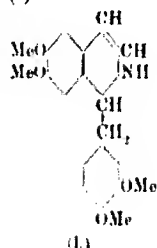
Since the combustion of this substance in a vacuum appears to lead to the formation of an unusually high percentage of nitric oxide, thus giving percentages of nitrogen somewhat above what could be accounted for on the average experimental error (in two cases 33.10 and 32.94 per cent. respectively), in the above analysis the volume of nitrogen was corrected for nitric oxide in a gas apparatus.

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CXX.—*iso*Quinoline Derivatives. Part V. The Constitution of the Reduction Products of Papaverine (continued).

By FRANK LEE PYMAN and WILLIAM COLEBROOK REYNOLDS.

IN Part II of this series (Trans., 1909, 95, 1616) it was shown by one of us that the amorphous base resulting from the reduction of papaverine is in reality tetrahydropapaverine, and it was further stated that Goldschmidt's so-called "tetrahydropapaverine" is 1:2 dihydropapaverine (I):



The reasons which led to this conclusion were as follows.

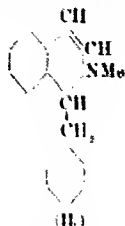
(1) Analyses and molecular weight determinations of the base and its derivatives prove that it has the formula  $C_{20}H_{23}O_4N$ , and its preparation by the reduction of papaverine,  $C_{20}H_{21}O_4N$ , therefore shows it to be a dihydropapaverine, unless it is obtained from an impurity in the papaverine, a possibility—at no time likely—which is definitely disproved in the present paper.

(2) The reactions of the base, for instance, the formation of a nitroso-derivative and benzoyl derivative, show that it contains an imino-group, therefore one of the additional hydrogen atoms occupies the 2 position of the *iso*quinoline ring.

(3) The resolution of the base by Pope and Peachey (Trans. 1898, 73, 893) proves it to contain an asymmetric carbon atom and on the assumption that this occupied the 1-position, as in alkaloids of the 1-benzyltetrahydro*iso*quinoline type (laudanosine, xaxotone, etc.), the position of the remaining hydrogen atom was fixed, and the base designated 1:2 dihydropapaverine.

This base, however, was a compound of considerable stability; its reduction could not be effected, and its *N*-benzoyl derivative was not readily attacked either by bromine or by sulphuric acid and manganese dioxide; its behaviour therefore differed from that of

1-benzyl-2-methyl-1:2-dihydroisoquinoline (II) (Freund and Beck, *Ber.*, 1909, **42**, 1762), a compound which may readily be reduced



to the corresponding tetrahydroisoquinoline, and which is easily attacked by oxidising agents.

This difference in behaviour was ascribed to the presence of a free imino-group in the former, and some corroboration of this view was adduced from the fact that Pictet and Athanasescu (*Ber.*, 1900, **33**, 2346), in preparing laudanoline by the reduction of papaverine hydrochloride, did not discover the *N*-methyl derivative of 1:2-dihydropapaverine. The present authors, however, now find that the reduction of papaverine methyl-salts leads to the production not only of laudanoline, but also of a new base,  $C_{21}H_{22}O_4N$ , which is shown to be the *N*-methyl derivative of 1:2-dihydropapaverine. Further, the new base is as stable as the parent compound; its reduction cannot be effected either by tin and hydrochloric acid or by sodium and amyl alcohol. It is therefore clear that the difference in behaviour between 1-benzyl-2-methyl-1:2-dihydroisoquinoline and 1:2-dihydropapaverine is not merely due to the influence of the imino-group in the latter, and the assumption that this base has the constitution represented by the term 1:2-dihydropapaverine does not appear to be justified without further experimental evidence.

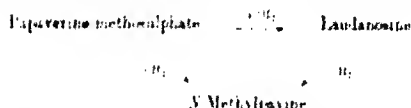
The further investigation of the constitution of this compound, however, more particularly with regard to the products obtained by its oxidation and degradation by complete methylation, is now in progress, and in order to avoid the use of a designation which may prove to be incorrect, it is proposed to adopt the name *pavine* for this base,  $C_{21}H_{22}O_4N$ , melting at  $201^{\circ}$ – $202^{\circ}$ , which has been termed "tetrahydropapaverine" by Goldschmidt (*Monatsh.*, 1886, **7**, 445; 1898, **19**, 324) and "1:2-dihydropapaverine" by Pyman (*loc. cit.*); the new base,  $C_{21}H_{23}O_4N$ , will therefore be *N*-methyl*pavine*.

*Pavine* is always formed together with tetrahydropapaverine in the reduction of papaverine with tin and hydrochloric acid, and has been so obtained by different workers using papaverine having

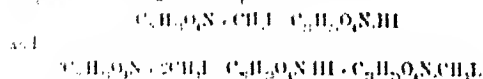


the correct melting point (Hofmann, Popo and Pearce, Pymann), but the yield is only small and varies from about 5 to 12 per cent of the theoretical; it appeared therefore to be possible, although unlikely, that pavine was derived from some impurity in the papaverine. In order to settle this point, the commercial papaverine used in these experiments was on one occasion very carefully purified, on methylation and subsequent reduction, a quantity of *N*-methylpavine was obtained together with laudanone, and it therefore follows that *N*-methylpavine is actually derived from *N*-methylpapaverine salts, and consequently that pavine is derived from papaverine.

*N*-Methylpavine is obtained by the reduction of papaverine methyl salts with tin and hydrochloric acid, together with laudanone, from which it can be readily separated by either of the methods given in the experimental part of this paper, it also formed to some extent in the oxidation of laudanone with chromic acid and manganese dioxide. The relation between these alkaloids is therefore as follows:



*N*-Methylpavine hydrochloride salts methodically are also formed together with pavine hydrochloride by the action of methyl salts on pavine according to the equations:



As in the case of pavine, so also in that of *N*-methylpavine, base and salts readily crystallise with a considerable amount of water on dilution.

## EXPERIMENTAL

### Purification of Papaverine.

After a preliminary experiment, in which besides laudanone a quantity of *N*-methylpavine was obtained by the reduction of papaverine methosulphate the papaverine required for the next experiment was very carefully examined.

The base melted at 146–147°, it was converted into the hydrochloride, and this salt crystallised twice from water, being obtained in monoclinic plates, which decomposed at 231° (corr.); on regeneration, the base was converted into the hydrogen oxalate and the salt crystallised twice from alcohol, when it separated

the rods, which decomposed at  $199^{\circ}$  (corr.), the base was then regenerated, but still melted at  $146\text{--}147^{\circ}$ , or  $147\text{--}148^{\circ}$  (corr.), and this melting point remained the same after recrystallization of a specimen of the base from benzene.\*

#### *Reduction of Papaverine Methosulphate.*

One hundred and eight-four grams of papaverine, which had been treated as above, were converted into the methosulphate (compare Decker and Fichorr, *Ber.*, 1904, **37**, 3401), and this was reduced with tin and hydrochloric acid in alcoholic solution, the conditions being similar to those previously adopted for the reduction of papaverine (Pyman, *Trans.*, 1903, **95**, 1614). After decomposition of the tin salts with hydrogen sulphide, and removal of the tin sulphide, the liquor was precipitated with sodium carbonate, filtered from the crude laudanose, and extracted with chloroform, the latter left on distillation a brown gum, which was dissolved in warm dilute hydrochloric acid, this solution on cooling deposited N-methylpavine hydrochloride in beautiful prisms. The crude laudanose was purified by crystallization as hydrogen oxalate, the mother liquors yielding, on regeneration of the base and crystallization of this as hydrochloride, a further quantity of N-methylpavine. Altogether 1.2 grams of laudanose and 9 grams of N-methylpavine hydrochloride were obtained.

The laudanose obtained in this manner melts at  $115\text{--}116^{\circ}$  (corr.), and the melting point is unchanged after recrystallization of the base from alcohol. The yield of pure laudanose is therefore 50 per cent. of the theoretical, Pictet and Athanasescu (*loc. cit.*) obtained 50 to 60 per cent.

*Laudanose hydrogen oxalate* crystallises from alcohol in microscopic needles, which contain  $1\frac{1}{2}\text{H}_2\text{O}$ , and, after drying at  $100^{\circ}$ , melts and decomposes at  $163\text{--}165^{\circ}$  (corr.), after sintering a few degrees earlier. After crystallisation from water, this salt contains  $2\text{H}_2\text{O}$ , and melts to a turbid, viscous liquid at  $80\text{--}85^{\circ}$  (corr.). It is sparingly soluble in cold water or alcohol.

0.1532 g. gave 0.329 g.  $\text{CO}_2$  and 0.0906  $\text{H}_2\text{O}$ .  $\text{C} = 58.1$ ,  $\text{H} = 6.6$ .

0.099 g. lost 0.0110 in a vacuum over  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{O} = 1.1$ .

$\text{C}_{11}\text{H}_{13}\text{O}_4\text{N} \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{C} = 58.2$ ,  $\text{H} = 6.7$ .

$\text{H}_2\text{O} = 5.7$  per cent.

$1.765^{\circ}$  lost 0.0155 at  $100^{\circ}$ .  $\text{H}_2\text{O} = 1$ .

$\text{C}_{11}\text{H}_{13}\text{O}_4\text{N} \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 9.1$  per cent.

\* In view of a recent publication by Fichter and Jovanovic (*Ber.*, 1910, **43**), it is of interest to note that, on treatment of the purified papaverine with distilled sulphuric acid, the crystals were, at first, a perfectly white solid, which, when dissolved in the acid, gave a yellow solution.

\* Air dried salt from alcohol.

\* Air dried salt from water.

*Separation of Laudanosine and N-Methylpavine.*

That the above method for the separation of laudanosine and *N*-methylpavine is fairly complete is shown by the following experiment.

A mixture of 10 grams of laudanosine and 1 gram of *N*-methylpavine, when converted into acid oxalate and recrystallised from water, gave 12.2 grams of laudanosine hydrogen oxalate; the base regenerated from the mother liquors then crystallised as hydrochloride gave 1.2 grams of *N*-methylpavine hydrochloride; on again regenerating the base from the mother liquors and crystallising as oxalate, another 0.9 gram of laudanosine hydrogen oxalate was obtained, and the last mother liquors gave a base yielding a small quantity of hydrochloride, which was not further worked up; the quantities recovered were equivalent to 9.5 grams of laudanosine and 0.9 gram of *N*-methylpavine.

Another method for the separation of the two bases depends on the different solubilities of the bases in alcohol.

A mixture of 10 grams of laudanosine and 1 gram of methylpavine crystallised from a minimum of hot alcohol gave 8.9 gram of laudanosine, the remainder converted into hydrochloride and crystallised from water gave 1.5 grams of *N*-methylpavine hydrochloride, and after regenerating the bases from the final mother liquor and crystallising from alcohol, a further 0.3 gram of laudanosine was obtained; the quantities recovered were the equivalent to 9.2 grams of laudanosine and 1.0 gram of *N*-methylpavine.

*N-Methylpavine, C<sub>20</sub>H<sub>27</sub>O<sub>4</sub>N*

This base is liberated in an amorphous condition when alkalis are added to aqueous solutions of its salts, but the precipitate becomes crystalline on keeping, and then forms colourless prisms which, after thorough drying in the air, contain  $1\frac{1}{2}$  to  $2\frac{1}{2}$  H<sub>2</sub>O. The hydrated base has no sharp melting point, but begins to soften at about 30°, gradually melts, and then effervesces at 100°; it loses nearly all its water of crystallisation when kept in a vacuum over sulphuric acid, and remains as a white, amorphous powder, which melts at about 90°.

0.1313 (air dried) lost 0.0389 in a vacuum over H<sub>2</sub>SO<sub>4</sub>. H<sub>2</sub>O = 2.96%  
C<sub>20</sub>H<sub>27</sub>O<sub>4</sub>N.2H<sub>2</sub>O requires H<sub>2</sub>O = 9.2 per cent.

0.1285 (dried in a vacuum) gave 0.3099 CO<sub>2</sub> and 0.1257 H<sub>2</sub>O  
C = 70.1, H = 7.1

After dehydration by boiling with benzene and anhydrous sodium sulphate, the base crystallises from benzene in hard prisms, which

anhydrous, and melt at  $140-141^{\circ}$  (corr.), after sintering a degree earlier; it crystallises from anhydrous ether in small, transparent prisms having the same melting point. It is sparingly soluble in water, ether, or light petroleum, but readily so in the other usual organic solvents. It dissolves in concentrated sulphuric acid, giving a pale yellowish green solution:

0.1555 gave 0.4035  $\text{CO}_2$  and 0.0995  $\text{H}_2\text{O}$ .  $\text{C}=70.8$ ;  $\text{H}=7.2$ .

0.1514 " 0.3922  $\text{CO}_2$  " 0.0971  $\text{H}_2\text{O}$ .  $\text{C}=70.6$ ;  $\text{H}=7.2$ .

0.1865 " 6.2 c.c.  $\text{N}_2$  at  $22^{\circ}$  and 758 mm.  $\text{N}=3.8$ .

0.2090 " by Zeisel's method, 0.5360  $\text{AgI}$ .  $\text{OMe}=33.9$ .

0.1529 " " " " 0.3915  $\text{AgI}$ .  $\text{OMe}=33.8$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4\text{N}$  requires  $\text{C}=70.9$ ,  $\text{H}=7.1$ ;  $4\text{OMe}=34.9$ ;

$\text{N}=3.9$  per cent.

The *hydrochloride* crystallises from water in large, colourless well-formed prisms, which melt at  $65-81^{\circ}$  (corr.), and contain 5 molecules of water of crystallisation, of which  $7\frac{1}{2}$  are lost on drying first in a vacuum, and then at  $100^{\circ}$ . This salt is soluble in about 50 parts of cold water, but easily soluble in hot water or alcohol:

0.5121 (air dried) lost 0.1293 at  $100^{\circ}$ .  $\text{H}_2\text{O}=25.2$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4\text{N} \cdot \text{HCl} \cdot 8\text{H}_2\text{O}$  loses  $7\frac{1}{2}\text{H}_2\text{O}$ . requires  $\text{H}_2\text{O}=25.2$  per cent.

0.1616\* gave 0.3707  $\text{CO}_2$  and 0.0972  $\text{H}_2\text{O}$ .  $\text{C}=62.6$ ;  $\text{H}=6.7$ .

0.1598\* " 0.3664  $\text{CO}_2$  " 0.0962  $\text{H}_2\text{O}$ .  $\text{C}=62.5$ ;  $\text{H}=6.7$ .

0.124\* " 0.0783  $\text{AgCl}$ .  $\text{Cl}=8.5$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4\text{N} \cdot \text{HCl} \cdot \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{C}=62.9$ ,  $\text{H}=6.8$ ,  $\text{Cl}=8.8$  per cent.

The *hydriodide* crystallises from water in large, nearly colourless prisms, which melt at  $70-87^{\circ}$  (corr.), and contain  $6\frac{1}{2}\text{H}_2\text{O}$ . It is easily soluble in hot water or alcohol. After drying, it has no sharp melting point, but gradually softens from about  $18^{\circ}$  onwards:

0.2194 (air dried) lost 0.0412 at  $100^{\circ}$ .  $\text{H}_2\text{O}=18.8$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4\text{N} \cdot \text{HI} \cdot 5\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}=18.3$  per cent.

0.1704\* gave 0.3242  $\text{CO}_2$  and 0.0815  $\text{H}_2\text{O}$ .  $\text{C}=51.9$ ,  $\text{H}=5.6$ .

0.1892\* " 0.0911  $\text{AgI}$ .  $\text{I}=26.0$ .

$\text{C}_{21}\text{H}_{20}\text{O}_4\text{N} \cdot \text{HI}$  requires  $\text{C}=52.2$ ,  $\text{H}=5.4$ ;  $\text{I}=26.3$  per cent.

The *aurichloride* crystallises from a mixture of acetone and absolute alcohol in terra cotta coloured needles, which contain a molecule of alcohol of crystallisation and decompose at  $19^{\circ}$  (corr.). It is almost insoluble in water or alcohol, but readily soluble in acetone:

0.2058† gave 0.2824  $\text{CO}_2$  and 0.0764  $\text{H}_2\text{O}$ .  $\text{C}=37.4$ ;  $\text{H}=4.2$ .

0.1722\* " 0.2686  $\text{CO}_2$  " 0.0665  $\text{H}_2\text{O}$ .  $\text{C}=37.4$ ;  $\text{H}=4.5$ .

\* Dried at  $100^{\circ}$ .

† Air dried salt.

0.2247 \* gave 0.0997 Au. Au = 26.5

0.6416 \* lost 0.0965 at 100°.  $C_2H_2O = 5.7$ .

$C_{11}H_{10}O_4N.HAuCl_4.C_2H_2O$  requires C = 37.2; H = 4.4; Au = 26.5  
 $C_2H_2O = 6.2$  per cent.

The *peracetic* crystalline from water in small, glistening, yellow needles, which melt at 219° (corr.), after sintering slightly from 200°. It is very sparingly soluble in cold water or alcohol:

0.1576 \* lost 0.0014 at 100°.  $H_2O = 0.9$ .

0.1735 † gave 0.3532  $CO_2$  and 0.0754  $H_2O$ . C = 55.5; H = 4.9.

$C_{11}H_{10}O_4N.C_4H_9O.N_2$  requires C = 55.5; H = 4.8 per cent.

The *methiodide* separates in colourless, glistening rods, which contain 2  $H_2O$ , and decompose at about 280° (corr.) on warming a methylalcoholic solution of the base with methyl iodide. It is sparingly soluble in cold water or hot alcohol:

0.5200 \* lost 0.6353 at 100°.  $H_2O = 6.8$ .

$C_{11}H_{10}O_4N.CH_3I.2H_2O$  requires  $H_2O = 6.8$  per cent.

0.1525 † gave 0.3036  $CO_2$  and 0.0792  $H_2O$ . C = 52.9; H = 5.7.

0.2318 † „ 0.1097 AgI. I = 25.6.

$C_{11}H_{10}O_4N.CH_3I$  requires C = 53.1; H = 5.7; I = 25.5 per cent.

After crystallisation from water, the methiodide forms beautiful large, clear prisms, which contain 4  $H_2O$ , and, after sintering from 111° and gradually becoming viscous, effervesce at 118–119° (corr.) after drying the fully hydrated salt at 100°; it has no sharp melting point, but begins to sinter at about 165° (corr.), and gradually becomes viscous and effervesces on raising the temperature:

0.1529 \* gave 0.3607  $CO_2$  and 0.0884  $H_2O$ . C = 46.5; H = 6.5.

0.2030 \* „ 0.0839 AgI. I = 22.1.

0.2716 \* lost 0.0326 at 110°.  $H_2O = 12.0$ .

$C_{11}H_{10}O_4N.CH_3I.4H_2O$  requires C = 46.4; H = 6.4; I = 22.3;  
 $H_2O = 12.7$  per cent.

The *methochloride* was prepared from the methiodide by double decomposition with silver chloride. It crystallises from water as beautiful, colourless prisms, which are sparingly soluble in water and melt at 75–99° (corr.). The air-dried salt contains 7  $H_2O$ , of which 6½ are lost at 100°; the dried salt sinters at 150–170°, and then effervesces:

0.5173 \* lost 0.1151 at 100°.  $H_2O = 22.4$ .

$C_{11}H_{10}O_4N.CH_2Cl.7H_2O$ , losing 6½  $H_2O$ , requires loss = 22.0 per cent.

0.1528 † gave 0.3599  $CO_2$  and 0.0987  $H_2O$ . C = 64.3; H = 7.2.

$C_{11}H_{10}O_4N.CH_2Cl.4H_2O$  requires C = 63.7; H = 7.1 per cent.

The *methohydride* was prepared by digesting a hot aqueous

\* Air-dried salt.

† Dried at 100°.

solution of the methiodide with silver oxide, filtering from silver oxide, and evaporating the liquor until crystals formed on the surface. On cooling, the base separated in large, transparent prisms, which melted and effervesced at about  $130^{\circ}$ . It contains a large and variable amount of water of crystallisation. It is very easily soluble in water, giving a strongly alkaline solution, which yields with aqueous potassium iodide a precipitate of the methiodide.

#### *Methylation of Pavine.*

Ten grams of pavine were dissolved in about 50 c.c. of chloroform, and gently warmed with 10 grams of methyl iodide, until a reaction began. A dark oil was deposited, and on keeping overnight, this became a mass of crystals, which were collected, washed with alcohol, and fractionally crystallised, first from absolute alcohol and then from water. The following products were obtained.

(1) 3.5 Grams of *N*-methylpavine methiodide. This salt effervesced at  $118-119^{\circ}$  (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance:

1636° gave 0.2819  $\text{CO}_2$  and 0.0931  $\text{H}_2\text{O}$ ; C = 47.0; H = 6.4.

1663° lost 0.0252 at  $100^{\circ}$ ;  $\text{H}_2\text{O}$  = 12.2.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{CH}_3\text{I} \cdot 4\text{H}_2\text{O}$  requires C = 46.4; H = 6.4;  
 $\text{H}_2\text{O}$  = 12.7 per cent.

(2) 7.0 Grams of *N*-methylpavine hydroiodide. This salt melted at  $170-81^{\circ}$  (corr.), and its melting point suffered no depression when the salt was mixed with the pure substance:

1635° gave 0.2374  $\text{CO}_2$  and 0.0822  $\text{H}_2\text{O}$ ; C = 42.2; H = 6.5.

1645° lost 0.0374 at  $100^{\circ}$ ;  $\text{H}_2\text{O}$  = 18.3.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{HI} \cdot 6\text{H}_2\text{O}$  requires C = 42.6; H = 6.5;  $\text{H}_2\text{O}$  = 18.3 per cent.

(3) 0.8 Gram of *pavine hydroiodide*. This salt softened about  $15^{\circ}$ , but did not melt until about  $26^{\circ}$ . After drying at  $100^{\circ}$ , it softens together at  $125^{\circ}$  (corr.) without really melting, and its melting point suffered no depression when the salt was mixed with the pure substance prepared by neutralising pavine with hydroiodic acid. This salt contains about  $4\text{H}_2\text{O}$ , and is sparingly soluble in cold water.

(4) Salt obtained in the methylation

1667° lost 0.0276 first in a vacuum, then at  $100^{\circ}$ ;  $\text{H}_2\text{O}$  = 14.0.

1658° gave 0.2950  $\text{CO}_2$  and 0.0740  $\text{H}_2\text{O}$ ; C = 51.0; H = 5.3.

(5) Salt obtained by neutralising pavine with hydroiodic acid

1643° lost 0.0228 first in a vacuum, then at  $100^{\circ}$ ;  $\text{H}_2\text{O}$  = 11.3.

\* Anhydrous.

\* Dried at  $100^{\circ}$ .

0.1546 g. gave 0.7501 CO<sub>2</sub> and 0.6735 H<sub>2</sub>O. C=51.2, H=5.3.

C<sub>10</sub>H<sub>15</sub>O<sub>3</sub>N.HI.3H<sub>2</sub>O requires H<sub>2</sub>O=10.3 per cent.

C<sub>10</sub>H<sub>15</sub>O<sub>3</sub>N.HI.3H<sub>2</sub>O " H<sub>2</sub>O=13.3 "

C<sub>10</sub>H<sub>15</sub>O<sub>3</sub>N.HI requires C=51.2; H=5.2 per cent.

A number of small fractions consisting of mixtures of the above were also obtained.

THE WELDON CHEMICAL WORKS,  
LOUGHBOROUGH.

### CXXI.—The Specific Rotatory Power of Hyoscyamine and the Relation between that of Alkaloids and their Salts.

By FRANCIS HOWARD CARR and WILLIAM COLERBROOK REYNOLDS.

In a recent communication Barrowcliff and Tutin (Trans., 1966, 95, 1966) have given  $[\alpha]_D^{25} = 32.1^\circ$  for the specific rotatory power of optically pure *d* and *l* hyoscyamine, deriving this figure by calculation from the values they obtained for the pure *d* and *l* hyoscyamine *d*-camphorsulphonates in aqueous solution. The being considerably higher than the figure generally accepted for hyoscyamine, namely,  $[\alpha]_D^{25} = 21^\circ$ , led them to conclude that optically pure hyoscyamine had hitherto been obtained, and they attributed the discrepancy to unavoidable racemisation occurring in the process of the regeneration of the base.

By fractional crystallization of a quantity of base having  $[\alpha]_D^{25}$  about  $-20^\circ$ , however, they obtained a fraction having  $[\alpha]_D^{25} = 25^\circ$ , and this was the highest rotatory power observed.

It has been shown by Gubiny and confirmed by Laidlaw that *d* and *l* hyoscyamine differ very considerably in their physiological properties, the *l*-isoisomeride being the more active. The question, therefore, of the specific rotatory power of pure hyoscyamine assumes considerable practical importance, for, according to the position defined by Barrowcliff and Tutin, the commercial product in general use is not the pure *l*-base possessing the highest possible physiological activity, but a mixture containing a considerable amount of the racemic base—atropine. Since the rotatory power of hyoscyamine affords the best means of determining its purity, no uncertainty must exist about the correctness of this constant.

In the course of extended experience in the preparation of

hyoscyamine, we have uniformly observed the specific rotatory power, of what we considered the pure base, to be about  $[\alpha]_D = 21^\circ$  (in dilute alcohol). By prolonged fractional crystallisation of both the camphorsulphonate and the alkaloid, we have not been able to obtain a base having a higher directly determined specific rotatory power than  $[\alpha]_D = 22.0^\circ$  (in dilute alcohol). That the latter was pure hyoscyamine was proved beyond all question by the following facts:

1) When the base of directly determined specific rotatory power  $[\alpha]_D = 22.0^\circ$  (in dilute alcohol) was neutralised, the value calculated for the basic ion rose to  $[\alpha]_D = 32.5^\circ$  (in aqueous solution), a figure almost identical with that deduced by Barrowcliff and Tutin.

2) It gave a *d*-camphorsulphonate, which, without purification, had  $[\alpha]_D = 7.7^\circ$ , again a value almost identical with that observed by Barrowcliff and Tutin for the salt on the specific rotatory power of which they founded their conclusions.

There remains to be explained the observation by Barrowcliff and Tutin of  $[\alpha]_D = 25.8^\circ$  (in dilute alcohol) for the specimen of hyoscyamine obtained by fractional crystallisation. In regard to this, these authors have very kindly furnished us with particulars of their procedure, which now admits, in view of our own observations as to the behaviour of hyoscyamine, of a perfectly simple explanation of their result. It appears that in determining the specific rotatory power of the specimen of base in question there was introduced into the alcohol (previously distilled over sodium hydroxide) with which the solution was prepared a small amount of acetic acid, with the object of counteracting any slight alkalinity, which might be expected to increase the rate of racemisation. The resulting solution therefore probably contained partly neutralised base, and in consequence gave a higher rotation than would have been the case if only free base had been present.

It also follows from the above mentioned facts that hyoscyamine does not, after all, possess any considerable susceptibility to racemisation, such as Barrowcliff and Tutin attributed to it.

We consider that there is no doubt whatever that the specific rotatory power of optically pure hyoscyamine is  $22.0^\circ$  (in 50 per cent. alcohol).

It is evident that Barrowcliff and Tutin arrived at an erroneous conclusion by assuming that the specific rotatory power of the base, as deduced from the molecular rotation of its salts in a dissolving solvent, would be identical, or nearly so, with that directly determined for the base, also in a dissolving solvent. Although this assumption may be legitimate in the case of many bases, there is no evidence to indicate that it is not invariably so, particularly



for tertiary bases, in which case are most of the naturally occurring alkaloids. For example, most of the alkaloids of the aconitine group are dextrorotatory, but their salts are levorotatory, whilst quinine and cocaine have each a lower specific rotatory power than their respective salts. It must not be overlooked, however, in regard to most of these cases that owing to differences of solubility of base and salt the published rotations of the former were made in alcohol of 70-100 per cent., whilst aqueous solutions of the salts were employed. From this it might be argued that the differences observed were attributable to incomplete ionisation in the case of the bases. Aconine and hyoscyne afford instances not open to this objection, the former having  $[\alpha]_D^{20} +23.0^\circ$  as base, and  $[\alpha]_D^{20} -55.7^\circ$  as salt, and the latter  $[\alpha]_D^{20} -28.0^\circ$  as base, and  $[\alpha]_D^{20} +32.7^\circ$  as salt, the determinations being made in aqueous solution in every case.

We believe that the distinction between the specific rotatory power of a base determined directly in a dissociating solvent and that deduced for the base ion from a determination of a salt has not been sufficiently appreciated. We have therefore considered it desirable to extend the investigation to a number of other alkaloids with the object of further supporting our contention as to the incorrectness of the principle above stated.

The alkaloids investigated were, besides hyoscyamine, the following: cocaine, codeine, hydrastine, nicotine, and quinine. The specific rotatory values of these were determined as base and base ion in the same dissociating solvent, which was either water or 70 per cent. alcohol, the former being used wherever the base was sufficiently soluble in it. The comparisons showed that all these bases without exception behave similarly to hyoscyamine, the two values obtained differing widely, as can be seen from the following table.

Alkaloid	Solvent	$[\alpha]_D^{20}$ of base (direct determination)	$[\alpha]_D^{20}$ of base ion (solution of a salt)
Cocaine	Water	-144.4	133.8
Nicotine	"	-78.0	+23.1
Hydrastine	70% alcohol	+112.0	+197.4
Cocaine	"	35.4	-77.7
Quinine	"	-170.5	262.1

We have also observed that whilst the specific rotatory power of the hyoscyamine base ion in aqueous solution (as a salt) was  $[\alpha]_D^{20} -32.5^\circ$  the value in 70 per cent. alcoholic solution was only  $[\alpha]_D^{20} -27.0^\circ$ . Although the work of many investigators, notably Pope and Prachay (Trans., 1899, 75, 1066), has shown that the rotation of a base is very considerably altered by the nature of

the solvent, it might be supposed that water and 50 per cent. alcohol, being dissociating solvents, would act alike. Since the values for hyoscyamine salts in water and in 50 per cent. alcohol differ somewhat widely, a similar comparison was made of other alkaloids and their salts, and it was shown that the respective values differ very considerably in almost every case. It follows that although 50 per cent. alcohol is a dissociating solvent, it must not be regarded as having the same influence upon the rotation as water. An attempt to trace the influence which the solvent is thus shown to exert upon the specific rotatory power of a number of bases and salts has led to some interesting results, which are recorded in the experimental part of this paper.

From the results obtained as to the influence of acids on the specific rotatory power of alkaloids of known constitution in dissociating solvents, it would appear that the differences cannot be attributed to structural change, and we suggest that the free alkaloids are either not ionised in solution at all, or only partly so, and that, whereas the basic nitrogen has a quinquevalent function in the salts, in the base it functions as trivalent even in aqueous solution. In other words, such bases do not form quaternary hydroxides with water as do ammonia and simple substituted ammonium bases.

#### EXPERIMENTAL.

##### *The Specific Rotatory Power of Hyoscyamine.*

Hyoscyamine *d*-camphotsulphonate was frequently recrystallised from acetone until no further change of melting point or specific rotation was effected; the base was then regenerated with ammonia and rapidly extracted with chloroform, the chloroform solution washed first with dilute ammonia and then with water, and evaporated in a vacuum at a low temperature. The base thus obtained, which gave  $[\alpha]_D^{20} = 21.7^\circ$  in 50 per cent. alcohol, was recrystallised twelve times from light petroleum (b. p.  $80-120^\circ$ ). It melted at  $107-105^\circ$ .

One gram, made up to 25 c.c. with 50 per cent. alcohol, gave, in a 2 dm. tube,  $\alpha_D = 1.765^\circ$ , whence  $[\alpha]_D^{20} = 22.06^\circ$ .

Since, during the last six crystallisations, the specific rotatory power was only increased by  $0.1^\circ$ , this substance must be regarded as pure. During the recrystallisation evidence was obtained of polymorphism, there being, in addition to the ordinary form, denser and larger crystals melting at  $102^\circ$ , which spontaneously change over to those having the higher melting point.

The rotation of hyoscyamine is not affected by the degree of concentration.

Four grams, made up to 20 c.c. with 50 per cent. alcohol, gave in a 1-dm. tube,  $\alpha_D = +1.41^\circ$ , whence  $[\alpha]_D = +22.0^\circ$ .

*The Specific Rotatory Power of L-Hyoscyamine Basic Ion.*

The specific rotatory power of L-hyoscyamine basic ion was determined by observing the rotation of the base dissolved in several dilute acids to neutrality. The results given in the following table show, as was of course expected, that the value for the basic ion is independent of the acid used.

Hyoscyamine, g.	Acid, grams per 100 c.c.	Length of tube	$[\alpha]_D$	$[\alpha]_D$ of basic ion
Hydrochloric acid	4.55	2 dm.	-2.82	-32.6
Sulphuric acid	4.60	"	-2.60	-32.4
Hydrobromic acid	4.9	"	-2.59	-32.4
Acetic acid	4.9	"	-2.6	-32.5

*The Specific Rotatory Power of d-Hyoscyamine.*

Some d-hyoscyamine was prepared from atropine by fractional crystallizing the d-camphorsulphonate in the manner described by Bartowich and Tutin (loc. cit.), and it was found that the rotations of the base and its neutral solutions agree with those recorded for the base, excepting that being more difficult to obtain quite free from the racemic form, the figures are somewhat lower than those observed for the latter.

One gram, made up to 25 c.c. with 50 per cent. alcohol, gave in a 2-dm. tube,  $\alpha_D = +1.05^\circ$ , whence  $[\alpha]_D = +21^\circ$ ; 1 gram, neutralized with sulphuric acid and made up to 25 c.c., gave, in a 2-dm. tube,  $\alpha_D = +2.50^\circ$ , whence  $[\alpha]_D = +31.25^\circ$ .

*The Effect of Concentration on the Specific Rotatory Power of d-Hyoscyamine d-Camphorsulphonate.*

It has been found that the rotation of pure d-hyoscyamine d-camphorsulphonate decreases as the concentration increases, as shown by the following result.

*l,l'-Hyoscyamine d-Camphorsulphonate.\**

Volume in 100 c.c.	Length of tube	$\alpha_D$	$[\alpha]_D$	$[M]$
20	2 dm.	-1.10	-5.5	27.55
10	"	-1.97	-9.85	32.1
12	"	-1.42	-7.1	35.16
8	"	-1.70	-8.5	39.67
4	"	-0.67	-3.35	45.65

These results, when plotted, form a straight line, from which the specific rotatory power at the point of greatest dilution is found to be  $[\alpha]_D = -9.1^\circ$ , whence  $[M]_D = 47.4^\circ$ .

As shown in the concluding part of this paper, this salt has a dextrorotation in chloroform solution, giving  $[M]_D + 9.9^\circ$ .

*Non-racemisation of the Base during Regeneration.*

The following experiment was carried out in order to see to what extent racemisation occurs during the process of regenerating hyoscyamine. Some hyoscyamine camphorsulphonate, which gave  $\alpha_D = -7.9^\circ$  in 7.5 per cent. aqueous solution, was converted into the base by the method previously described. The base gave  $\alpha_D = -22.3^\circ$  in 50 per cent. alcohol. One gram of this base was combined with the quantity of *d*-camphorsulphonic acid which by previous titration was found to be required (owing to the fact that *d*-camphorsulphonic acid retains water of crystallisation, this procedure was necessary), namely, 0.8408 gram, and made up to 25 c.c., making a solution equivalent to 1.803 grams of hyoscyamine *d*-camphorsulphonate in 25 c.c. This solution gave, in a 2 dm. tube,  $\alpha_D = -1.11^\circ$ , whence  $[\alpha]_D = -7.7^\circ$ . It is thus proved that the alkaloid suffered no loss of rotatory power during the process.

*The Influence of Neutralisation on the Specific Rotatory Power of Alkaloids.*

The change of specific rotatory power, which is brought about when an alkaloid is neutralised, was determined in several instances, employing the same solvent for both base and salt. The results,

\* Barrowcliff and Tutin (*loc. cit.*), in calculating the specific rotatory power of *l,l'*-hyoscyamine from the above salt, employed the figure  $[M]_D + 51^\circ$  for the specific rotatory power of the *d*-camphorsulphonic ion. Pope and Peachey (*Trans. Faraday Soc.*, 1948, 44, 1044) gave  $[M]_D + 51.7^\circ$ ; but in a private communication, Prof. Pope informs us that more recent determinations have afforded a somewhat lower result.

From a large number of determinations of the specific rotatory power of pure hyoscyamine camphorsulphonate, we have obtained as a mean result  $[\alpha]_D = -20.1^\circ$ , whence  $[M]_D = +50.05^\circ$ , but this figure is subject to considerable variation according to temperature.

which are recorded in the table on p. 1335, show that the rotation is sometimes increased and sometimes diminished, there being change in every case which we have investigated.

*The Influence of the Solvent on the Specific Rotatory Power of Alkaloids.*

Owing to the insolubility of many alkaloids in water, 50 per cent. alcohol has been employed in determining the rotations of the insoluble ones. In order to determine whether this solvent may be regarded as having the same effect as water, comparisons have been made employing water and 50 per cent. alcohol for dissolving the alkaloids or salts. The differences, which in some cases are considerable, are given in tabular form:

	Solvent: Water			Solvent: 50 per cent. alcohol		
	Length of tube of per cent. 100 c. c.	$\alpha_D$	$[\alpha]_D$	Length of tube of per cent. 100 c. c.	$\alpha_D$	$[\alpha]_D$
<i>Alkaloids</i>						
Sol. in H <sub>2</sub> O, 2 dm. 1.008	1.75	81.8	2 dm. 1.048	-1.69	77.2	4.1
Hydrastine base						
" with HCl	2.0	+0.12	+15.0	1.643	+0.47	+197
Hyoscyamine						
" neutralized with H <sub>2</sub> SO <sub>4</sub>	4.0	-2.62	-32.6	4.0	-2.16	-27.0
Scutellaria	4.0	-1.47	-17.2	4.0	-1.06	-10.2
<i>Alkaloid salts</i>						
" with H <sub>2</sub> PO <sub>4</sub>	4.0	-2.11	-26.4	4.0	-2.07	-262.1

Since the addition of an equal weight of alcohol to the water modifies the specific rotatory power, the addition of larger proportions might be expected to produce further change.

Hydrastine, which has a strong dextrorotation in 50 per cent. alcohol, is optically inactive in 95 per cent. alcohol, and levorotatory in 100 per cent. alcohol; a similar change occurs when acetone is employed as the solvent.

A striking experiment bearing on this point is recorded in the following table:

*Hydrastine.*

Solvent	Length of tube	Concentration	$\alpha_D$	$[\alpha]_D$
50 per cent. alcohol	2 dm.	0.201	-0.47	+115.0
95 " "	"	0.2	+0.15	+37.5
93 " "	"	0.2	+0.12	+30.0
91 " "	"	0.4	0.0	0.0
87 " "	"	0.4	-0.10	-12.5
100 " "	"	0.291	-0.29	-45.8
<i>Alkaloid salts</i>				
Hydrastine with water	"	0.2	0.40	+100.0
Acetone and quinine	"	4.0	6.80	+50.0

TABLE I  
Specific rotation of solutions of a salt

Alkaloid	Solvent	Grams per 100 c.c.	$\alpha_D$	[ $\alpha$ ] <sub>D</sub>	[M] <sub>D</sub>	Weighed as calculated as base	Grams of base per 100 c.c.	$\alpha_D$	[ $\alpha$ ] <sub>D</sub>	[M] <sub>D</sub>	Arithmetical difference of [M] <sub>D</sub> of base and salt
Cocaine	50% alcohol	1.544	-0.77	-35.4	-107.3	Hydrochloride calculated as base	0.3569	5.60	-78.5	-238.0	130.7
Cocaine	Water	0.2	-2.22	-111.1	63.1	Base, 30% alcohol by H <sub>2</sub> SO <sub>4</sub>	2.0	5.35	132.4	-600.0	31.8
Hyoscyamine	20% alcohol	4.0	-1.765	-22.9	65.6	Base, 30% alcohol by H <sub>2</sub> SO <sub>4</sub>	4.0	2.16	-27.0	78.0	34.4
Hyoscyamine	50% alcohol	0.204	0.47	-115.2	64.2	H <sub>2</sub> SO <sub>4</sub> base, 30% calculated as base	1.665	4.64	-127.0	-754.0	312.0
Nicotine	Water	4.225	-7.67	77.9	-126.2	Base, 30% alcohol by H <sub>2</sub> SO <sub>4</sub>	4.26	2.29	-23.1	-37.4	163.6
Cocaine	50% alcohol	4.0	-0.764	-111.1	65.3	Base, 30% alcohol by H <sub>2</sub> SO <sub>4</sub>	4.0	-25.97	-262.1	-649.0	297.9

Temperature 20.0 C. Note: The values of base were all 100% based on the anhydrous condition.

*Modifying Influence of Different Acidic and Basic Groups on the Specific Rotatory Power of Bases and Acids in Dry Chloroform*

The molecular rotatory power of an alkaloid and its different salts in anhydrous chloroform, where dissociation cannot occur, may be expected to vary, since the salt remains in the molecular condition. Such is shown to be the case. Where different acids are employed to neutralise the base, the rotation value differs. The results recorded in the following table bear upon this point:

*Comparison of the Specific Rotation of Alkaloids and their Salts in Dry Chloroform,  $l = 2 \text{ dm.}$* 

	Free base			Anhydrous salt		
	Grams per 100 c.c.	$[\alpha]_D^{25}$	(M)	Grams per 100 c.c.	$[\alpha]_D^{25}$	(M)
Cocaine	1	126	15.75	Hydrochloride	2	+240
Mecamylamine	1	129	23.75	[Base neutralised by HCl and dried]	4	-278
Hydroxycine	2	155	27.4	Hydrochloride	2	+452
				Sulphate	2	+744
				Acetosalate	2	+822

The above results point to the modifying influence which the presence of different acid groups has on the rotation value of the asymmetric carbon atom of the base. A similar influence is produced on the asymmetric carbon atom of the acid by combination with different bases. This has been proved by determining the rotatory power in dry chloroform of the active and inactive camphorsulphonates of various alkaloids and taking the difference. This method affords a means of determining what proportion the optical activity of the active salt of an active base is due to the respective basic and acidic parts of the molecule. The observations referred to are recorded in the following table:

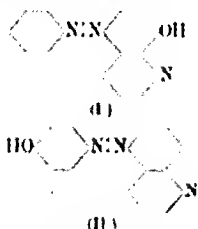
Camphor sulphonate of	[M] in chloroform.		Difference due to difference in sulphonic residue
	Salt of d acid	Salt of dl acid	
Cocaine	50.0	202.5	152.5
Cocaine	93.1	228.0	128.9
12-Bromocamphoramine	+9.9	107.0	116.9
Atropine	+114.2	0.0	114.2
Hydroxycine	+962.0	+791.0	171.0
Ephedrine	+157.9	0.0	157.9

THE WELLS-CORRE CHEMICAL WORKS,  
DARTFORD, KENT.

## CXXII.—p-Hydroxyazo-derivatives of Quinoline. Part I.

By JOHN JACOB FOX.

The hydroxyazo-derivatives of 8-hydroxyquinoline are of especial interest, as they contain a fairly basic group in the ortho position with respect to the hydroxyl group. It was expected that this would have a profound effect on the acidic properties of the hydroxyazo-compounds obtained. As a matter of fact, none of the compounds containing the hydroxyl group in the quinoline nucleus could be acetylated even after prolonged boiling with acetic anhydride and anhydrous sodium acetate, and it was not found possible to prepare the methoxy derivatives by boiling with methyl anhydride and sodium methoxide. Monohydrochlorides could be readily prepared, but the dihydrochlorides to which the oxonium salt feature is attributable (Hewitt and Fox, *Trans.*, 1908, **93**, 333) are very unstable, and could only be preserved in an atmosphere of hydrogen chloride. In all these respects the compounds differ strikingly from the simple hydroxyazo-compounds, such as benzene azophenol or benzeneazo- $\alpha$ -naphthol. In order to ascertain whether the basic character of the quinoline nucleus affected the molecule as a whole, or whether the presence of the basic group in the ortho position with respect to the hydroxyl group was the factor which prevented acetylation and alkylation of the hydroxyl group at the 8 position, compounds were prepared in which the hydroxyl group was no longer in the quinoline nucleus. The simplest of the six kinds of compounds are indicated by the formulae:



Whilst the compound represented by formula I could not be acetylated even when dissolved in pyridine, compound II was found to undergo acetylation and alkylation with ease, as in the case with benzeneazophenol. The only explanation of the circumstance which seemed to meet all the facts is that the hydroxyl group in I is



prevented from exerting its normal activity by the presence of a strongly basic group in its neighbourhood.

The possibility of the compounds being quinonehydrazones would not agree with the observed behaviour, since then acetylation or alkylation should take place readily. The instability of the hydrochloride of the type I, as compared with that of type II, is better explained as due to the formation of oxonium salts rather than carbonium salts, for if stable carbonium salts can be formed in II by the carbon atom, in the benzene nucleus para- with respect to the *azo* grouping, there appears to be no reason why even more stable salts should not also be formed by I.

Both types of substance are true hydroxyazo-compounds, judged from the absorption spectra of the solutions in alcohol; for although some variation in the persistency of the main band occurs (curve, p. 1344), the head of this band, both with 5-benzeneazo-8-hydroxyquinoline and quinolineazo-phenol, occurs at about  $\lambda$  2600,  $\mu$ , as in the case of aminobenzeneazo-phenol (Hewitt and Thomas, *Trans.* 1902, **95**, 1225), which also contains a basic group in the molecule. In the extreme case of a basic hydroxyazo-compound such as quinolineazo-hydroxyquinoline, the absorption spectrum gives the head of the band at  $\lambda$  2500 about, although the persistency is much diminished (curve, p. 1348). A consideration of the properties of the series of compounds described (for example, the formation of dihydrochlorides and hydrates, the colours obtained by dissolving in strong mineral acids and the position of the head of the main bands in the absorption spectra) shows that even in these compounds, in which from the presence of the basic quinone nucleus the possibility of quinone-hydrazone formation was increased, no such change from the true hydroxyazo-structure has taken place.

#### EXPERIMENTAL

The *p*-hydroxyazo-derivatives of quinoline described here were prepared in the usual way from the diazonium chlorides and solutions of 8-hydroxyquinoline in aqueous sodium hydroxide. Matheson stated that he had prepared benzeneazo-hydroxyquinoline, *p*-tolueneazo-hydroxyquinoline, and *p*-bromobenzeneazo-hydroxyquinoline (*Ber.* 1888, **21**, 1642), but it was impossible to repeat the work for his description, as no melting points are given, and the properties of the substances are inadequately described. I therefore prepared these three derivatives amongst the others, and descriptions will be found below. All the azo-derivatives of 8-hydroxyquinoline give sparingly soluble sodium salts, which separated from the alkaline solutions after some hours. It was necessary to allow the combination to proceed for twelve hours or longer, as otherwise some unchanged

hydroxyquinoline was obtained. The fact that the sodium salt of 8-hydroxyquinoline is hydrolysed to a greater extent than that of phenol (this vol., p. 1119) is doubtless the cause of the slow combination. The insolubility of the sodium salts furnished a ready method of purifying the hydroxyazo-compounds, as any unchanged substance would remain in solution in the alkaline liquid.

### 5-Benzeneazo-8-hydroxyquinoline.

The benzenediazonium chloride solution, prepared from 14.7 grams of aniline, was poured into an aqueous sodium hydroxide solution containing 22 grams of 8-hydroxyquinoline. After eighteen hours the insoluble red sodium salt was collected, washed with water, decomposed with dilute acetic acid, washed with water, dried, and powdered. The powdered material crystallised best from alcohol in clusters of needles of chocolate-brown colour (m. p. 171°). The compound dissolved in chloroform, pyridine, benzene, and the usual organic solvents.

0.2144 gave 0.5668  $\text{CO}_2$  and 0.0898  $\text{H}_2\text{O}$ .  $\text{C}$  72.1;  $\text{H}$  4.65.

0.1760 „ 26.0 c.c.  $\text{N}_2$  at 20° and 764 mm.  $\text{N}$  17.2.

$\text{C}_{15}\text{H}_{11}\text{ON}_3$  requires  $\text{C}$  72.3;  $\text{H}$  4.4;  $\text{N}$  16.9 per cent.

Some of the powdered material was mixed with anhydrous sodium acetate and boiled for several hours with acetic anhydride, the product was poured into alcohol, diluted with water after some time, and the precipitate collected and washed. The crude product did not melt sharply, but on recrystallising twice from alcohol it melted at 170°, and when mixed with the original substance showed no depression of melting point. Similar results were obtained when a pyridine solution of the substance was boiled with acetic anhydride. It is clear that if any acetylation occurs, the acetyl derivative formed is very small in amount, for the main quantity of material is recovered unchanged.

An attempt was made to methylate the compound by heating a solution in methyl alcohol, containing sodium methoxide, with methyl iodide. The product obtained crystallised from alcohol, and melted at 170°; when mixed with the original substance, no change in melting point was observed. The experiment was repeated with the silver salt; but although in this case the crude product softened at a lower temperature than the melting point, recrystallisation from alcohol again yielded the original material. As this suggested considerable hydrolysis of the salts, the sodium salt was prepared. It was not possible to obtain this salt pure, since the neutral salt was hydrolysed by water, and a determination of sodium gave only about 90 per cent. of the required amount. The silver salt was

prepared by dissolving the compound in the calculated amount of alcoholic sodium hydroxide, and adding an alcoholic solution of silver nitrate. A purple salt was precipitated, which was collected, washed with water, and then with hot alcohol. It became much darker on washing with alcohol, and yielded an amount of silver considerably in excess of that required for the neutral salt, indicating that the salt had been decomposed by the alcohol and the acid removed, leaving excess of silver.

It was important to examine the salts of benzeneazohydroxyquinoline acting as a base in order to ascertain whether salts of the normal azine type were formed, and some of these were prepared. The hydrochloride was prepared by evaporating a solution of the base in concentrated hydrochloric acid until crystals formed. After setting aside for some time, the crystals were collected, and washed with a little strong acid. The *hydrochloride* was obtained as a mass of dark red needles, but, if concentrated too rapidly, as an almost black, crystalline mass of plates, melting at 223°. The substance retains all its hydrogen chloride at 100°.

0.2482 gave 0.1258 AgCl. Cl = 12.5.

$C_{12}H_{11}ON_2HCl$  requires Cl = 12.4 per cent.

The *zinc salt* was obtained by evaporating a solution of the hydrochloride with excess of hydrochloric acid and zinc chloride until crystals began to form; these consisted of dark red needles.

0.5366 gave 0.0602 ZnO. Zn = 8.9.

0.2694 " 0.1588 AgCl. Cl = 19.1.

$C_{12}H_{11}ON_2HCl \cdot ZnCl_2$  requires Zn = 9.2; Cl = 20.6 per cent.

This salt is probably hydrated.

*Platinichloride*. An alcoholic solution of the hydrochloride was mixed with a solution of chloroplatinic acid. A dark, chocolate coloured, microcrystalline precipitate formed:

0.3166 gave 0.0752 Pt. Pt = 21.8.

$C_{12}H_{11}ON_2 \cdot H_2PtCl_6$  requires Pt = 21.5 per cent.

The dihydrochloride could not be isolated from a solution in chloroform, for although a dark purple precipitate resulted on adding in hydrogen chloride, the salt fumed strongly in the air, and analysis showed that the final product did not contain sufficient chlorine for the dihydrochloride. The salt is therefore much more unstable than the corresponding derivatives of benzeneazo- $\alpha$ -naphthol, and was finally prepared by passing hydrogen chloride over a weighed quantity of substance in a stoppered tube and determining the increase of weight, the apparatus being weighed full of hydrogen chloride before and after passing in the gas. The resulting salt was dark violet, almost black:

0.1606 benzeneazohydroxyquinoline absorbed 0.0483 HCl.

Increase = 30.4.

$C_{10}H_{11}ON_3$  requires increase = 28.3 per cent.

As stated above, this salt fumes in the air, and the loss of weight was only about three-quarters of that required for a loss of one molecule of hydrogen chloride; it was found that this was due to the formation of a hydrate in moist air, and in this respect the substance behaves like other hydroxyazo compounds (Hewitt, *Ber.*, 1905, 28, 799):

0.1502 gave 0.1900 substance after being subjected to action of hydrogen chloride, and keeping all night in moist air; AgCl obtained from this 0.0932 Cl = 12.1.

$C_{10}H_{11}ON_3 \cdot HCl \cdot \frac{1}{2}H_2O$  requires Cl = 12.0 per cent.

An attempt was made to combine benzeneazohydroxyquinoline with ethyl iodide. Under the ordinary pressure no combination occurred, whilst heating in a sealed tube with ethyl alcohol and ethyl iodide at 100° or 120° yielded a brownish black, crystalline mass of needles, which, on recrystallisation from alcohol, did not melt below 274°. The substance gave only a brown solution in concentrated sulphuric acid instead of the deep magenta of the original:

0.1502 gave 0.2182  $CO_2$  and 0.0412  $H_2O$ . C = 39.6; H = 3.05.

0.1674 .. 15.5 c.c.  $N_2$  at 22° and 763 mm. N = 10.1.

0.1922 .. 0.1660 AgI. I = 46.7.

The total of the four constituents is 99.7, so that the substance contains practically no oxygen. Treatment with potassium hydroxide failed to remove the iodine, and boiling with zinc and acetic acid effected practically no change in colour. Similar results were obtained with methyl iodide, but in this case a violent outrush of gas resulted on opening the sealed tubes. The substances obtained were not investigated further, but they are obviously not derivatives of hydroxyazoquinoline. The addition of alkyl iodides could not be effected in any of the azo derivatives of the hydroxyquinoline.

#### 5 p-Toluenazo-8-hydroxyquinoline.

Prepared from p-toluenediazonium chloride and an alkaline solution of 8-hydroxyquinoline. The insoluble sodium salt was removed, decomposed with acetic acid, washed and dried. The product crystallised from chloroform in chocolate-brown needles, melting at 153°, and was readily soluble in organic solvents:

0.1702 gave 0.4568  $CO_2$  and 0.0768  $H_2O$ . C = 73.2; H = 5.0.

0.1410 .. 19.7 c.c.  $N_2$  at 18° and 762 mm. N = 16.1.

$C_{12}H_{13}ON_3$  requires C = 73.9; H = 4.9; N = 16.0 per cent.

Attempts to acetylate or methylate failed, as in the case of benzeneazohydroxyquinoline.<sup>8</sup>

The substance obtained after prolonged heating with acetic anhydride melted at 173°, and gave 16.4 per cent. of nitrogen, agreeing with unchanged tolueneazohydroxyquinoline.

The hydrochloride, prepared by heating with concentrated hydrochloric acid, consisted of scarlet needle-shaped crystals; another preparation consisted of almost black plates, but was probably impure.

0.1908 gave 0.0796 AgCl. Cl = 11.7.

$C_{16}H_{11}ON_3HCl$  requires Cl = 11.85 per cent.

This and all other hydrochlorides are readily hydrolysed. It was found that a solution in concentrated hydrochloric acid, when diluted with water until a concentration of 1.5*N* acid was reached, gave a precipitate of the base free from halogen.

Dihydrochloride: 0.2916 absorbed 0.0832. HCl = 28.2.

$C_{16}H_{11}ON_3 \cdot 2HCl$  requires increase = 27.6 per cent.

The salt consists of a violet-black powder.

The sodium salt consisted of fine red needles, but, after washing, contained too little sodium for the neutral salt. The silver salt yielded too much silver: 32.4 per cent., against 29.2 for the neutral silver salt.

The zinc salt gave Zn = 8.4 per cent., agreeing with the formula  $(C_{16}H_{11}ON_3HCl)_2 \cdot ZnCl_2$ , and consisted of red needle-shaped crystals.

The platinum chloride  $(C_{16}H_{11}ON_3)_2 \cdot H_2PtCl_6$  contained Pt = 22.5 (calc.) Pt = 20.9 (per cent.), and was prepared as directed for benzeneazohydroxyquinoline.

### 5-*p*-Bromobenzenediazo-8-hydroxyquinoline.

A solution of *p*-bromobenzenediazonium chloride was poured into an alkaline solution of 8-hydroxyquinoline, and the sodium salt collected, decomposed, and washed as above; it crystallised from chloroform in very small, reddish-brown needles, melting at 21°. The substance dissolves sparingly in alcohol or benzene, but readily in pyridine and other solvents.

0.1508 gave 0.3024 CO<sub>2</sub> and 0.0434 H<sub>2</sub>O. C = 54.6; H = 3.25.

0.1614 .. 17.7 c.c. N<sub>2</sub> at 18° and 762 mm. N = 12.9.

0.3178 .. 0.1814 AgBr. Br = 24.6.

$C_{15}H_{10}ON_3Br$  requires C = 54.9; H = 3.1; N = 12.8;

Br = 24.4 per cent.

The compound cannot be acetylated or methylated. An attempt to combine it with methyl iodide yielded an unworkable tar.

A monohydrochloride, consisting of small, bright red plates

melting at 246°, separated from a solution in concentrated hydrochloric acid.

The *dihydrochloride*—0.1708 absorbed 0.0414 HCl. Increase = 1.2 (calc., increase = 22.3 per cent.). Keeping in moist air resulted in loss of hydrogen chloride, and the final increase in weight was 11.2 per cent.:

$C_{15}H_{10}ON_2Br, HCl, \frac{1}{2}H_2O$  requires increase = 13.8 per cent.

*5-p-Nitrobenzenazo-8-hydroxyquinoline.*

Prepared from *p*-nitrobenzenediazonium chloride and an alkaline solution of 8-hydroxyquinoline. The alkaline solution of the substance was of a deep blue colour (almost black). It resembles other nitrohydroxyazo-compounds in being sparingly soluble in most organic solvents. It crystallised from pyridine or chloroform in chocolate-coloured, microcrystalline needles, melting at 281°.

0.1522 gave 0.3428  $CO_2$  and 0.0502  $H_2O$ . C 61.4; H 3.7.

0.1488 „ 24.1 c.c.  $N_2$  at 19° and 765 mm. N 18.9.

$C_{15}H_{10}O_2N_2$  requires C 61.2; H 3.4; N 19.0% per cent.

A *monohydrochloride* was prepared as above, and crystallised in deep red needles, which did not melt below 281°.

0.2768 gave 0.1266  $AgCl$ . Cl 11.3.

$C_{15}H_{10}O_2N_2, HCl$  requires Cl 10.7 per cent.

The sodium salt is sparingly soluble.

*5-p-Acetylaminobenzenazo-8-hydroxyquinoline.*

Prepared from *p*-acetylaminobenzenediazonium chloride and an alkaline solution of 8-hydroxyquinoline. The substance is soluble in most organic solvents, but not in benzene or ether. It crystallised from pyridine in deep yellow plates, melting and decomposing at 260°.

0.1512 gave 0.3681  $CO_2$  and 0.0666  $H_2O$ . C 66.5; H 4.9.

0.1414 „ 22.4 c.c.  $N_2$  at 17° and 758 mm. N 18.5.

$C_{17}H_{14}O_2N_2$  requires C 66.7; H 4.6; N 18.3 per cent.

The compound cannot be acetylated. It yields an orange-yellow sodium salt.

*5-p-Aminobenzenazo-8-hydroxyquinoline.*

Prepared by boiling the foregoing acetyl derivative for two hours with a large excess of 20 per cent. hydrochloric acid. The compound was soluble in the usual organic solvents, and crystallised from 50 per cent. aqueous alcohol in dark brown needles, melting and decomposing at 207°. Addition of dilute hydrochloric acid to an alcoholic solution gives a yellow solution; more acid renders the

solution red. These changes are probably connected with the formation of mono- and dihydrochlorides:

0.1671 gave 0.4646 CO<sub>2</sub> and 0.0669 H<sub>2</sub>O. C=68.0; H=4.6.

0.1292 " 21.3 c.c. N<sub>2</sub> at 21° and 761 mm. N=21.5.

C<sub>12</sub>H<sub>10</sub>ON<sub>2</sub> requires C=68.2; H=4.5; N=21.2 per cent.

The *dihydrochloride*, prepared by evaporation of a solution concentrated hydrochloric acid, forms chocolate-coloured needles which do not melt below 281°.

0.2552 gave 0.2184 AgCl. Cl=21.2.

C<sub>12</sub>H<sub>10</sub>ON<sub>2</sub>·2HCl requires Cl=21.0 per cent.

A *trihydrochloride* can be formed by passing hydrogen chloride over the base in a closed vessel; it consists of a dark purple powder.

0.1584 absorbed 0.0672 HCl. Increase=42.4.

C<sub>12</sub>H<sub>10</sub>ON<sub>2</sub> requires increase=41.5 per cent.

The *platinichloride*, prepared in the usual way, consists of a dark brown, microcrystalline powder.

0.2488 gave 0.0736 Pt. Pt=29.2

C<sub>12</sub>H<sub>10</sub>ON<sub>2</sub>·H<sub>2</sub>PlCl<sub>6</sub> requires Pt=26.9 per cent.

#### 5p-Ethoxybenzenesulfo-8-hydroxyquinoline.

Prepared from diazotised p-phenetidine hydrochloride and an alkaline solution of 8-hydroxyquinoline. The red *sodium salt* was collected, and treated as above. The azo compound dissolves in the usual solvents, and crystallises from chloroform in brown needles having a green reflex, and melting at 176–177°.

0.1592 gave 0.3812 CO<sub>2</sub> and 0.0634 H<sub>2</sub>O. C=69.4; H=5.1.

0.1290 " 16.0 c.c. N<sub>2</sub> at 22° and 761 mm. N=14.7.

C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> requires C=69.6; H=5.1; N=14.3 per cent.

The *hydrochloride*, prepared by evaporation with concentrated hydrochloric acid, separates in chocolate-brown needles, melting at 227°.

0.1888 gave 0.0884 AgCl. Cl=11.6.

C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>·HCl requires Cl=11.9 per cent.

Hydrogen chloride passed over the base gave the following results.

0.1562 gained 0.0548 HCl. Increase=35.1.

C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>·2HCl requires increase=24.9 per cent.

C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>·3HCl " increase=37.4 "

The substance therefore tends to form a trihydrochloride.

In order to ascertain whether the azo-compounds of this class were para-hydroxy compounds, the dye was reduced by tin and hydrochloric acid, and the tin removed by hydrogen sulphide. The solution was evaporated to small bulk with hydrochloric acid

separated from some fatty matter, neutralised with sodium carbonate, and rendered slightly acid with sulphuric acid. After some hours the characteristic tufts of colourless, silky needles of 5-amino-8-hydroxyquinoline sulphate described by Fischer and Renouf (*Ber.*, 1884, 17, 1642) separated.

*5-n-Naphthaleneazo-8-hydroxyquinoline.*

A solution of  $\alpha$ -naphthalenehazanium chloride was poured into an alkaline solution of 8-hydroxyquinoline. The reddish brown sodium salt was decomposed with acetic acid, and the product washed and dried. The material was best purified by repeated washing with alcohol, the residue being found to be pure. With some difficulty, microcrystalline chocolate coloured needles, melting at 252–253°, were obtained from benzene. The compound dissolves sparingly in organic solvents. It is noteworthy that the solution of the substance in concentrated sulphuric acid is deep blue.

0.1042 gava 0.2922  $\text{CO}_2$  and 0.0378  $\text{H}_2\text{O}$ .  $\text{C} = 76.5$ ;  $\text{H} = 4.0$ .

0.1688 „ 20.5 c.c.  $\text{N}_2$  at 19° and 762 mm.  $\text{N} = 14.15$ .

$\text{C}_{19}\text{H}_{13}\text{ON}_2$  requires  $\text{C} = 76.25$ ;  $\text{H} = 4.35$ ;  $\text{N} = 14.0$  per cent.

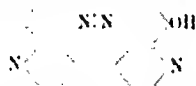
This substance cannot be acetylated.

The *hydrochloride*, prepared by evaporation with hydrochloric acid, occurs in reddish-brown, microcrystalline needles:

0.1828 gava 0.0802  $\text{AgCl}$ .  $\text{Cl} = 10.85$ .

$\text{C}_{19}\text{H}_{13}\text{ON}_2\cdot\text{HCl}$  requires  $\text{Cl} = 10.6$  per cent.

*Quinolizato-8-hydroxyquinoline.*



10.8 Grams of 5-aminoquinoline dihydrochloride were diazotised and poured into an alkaline solution of 7.2 grams of 8-hydroxyquinoline. The red sodium salt was decomposed with acetic acid, the product washed, dried, and boiled several times with alcohol. The compound is slightly soluble in benzene and insoluble in ether, but dissolves to a somewhat greater extent in other solvents. It separates from a solution in chloroform as an amorphous, dirty brown powder, melting and decomposing at 268°. The solution in alcohol is reddish yellow; a drop of dilute hydrochloric acid produces a bright yellow solution, and further addition of acid changes the colour to a deep orange shade. No acetyl compound could be obtained. Heating under pressure with methyl iodide yielded a



tarry mass and gaseous products. Prolonged boiling under the ordinary pressure with methyl alcohol and methyl iodide resulted in the formation of a small quantity of material containing halogen, but the amount was too small for further examination:

0.1432 gave 0.3802  $\text{CO}_2$  and 0.0536  $\text{H}_2\text{O}$ .  $\text{C}=72.4$ ;  $\text{H}=4.2$ .

0.1325 " 21.4 c.c.  $\text{N}_2$  at  $20^\circ$  and 760 mm.  $\text{N}=19.0$ .

$\text{C}_{10}\text{H}_{11}\text{ON}_4$  requires  $\text{C}=72.0$ ;  $\text{H}=4.0$ ;  $\text{N}=18.7$  per cent.

The *dihydrochloride* prepared by evaporation with concentrated hydrochloric acid, consists of magenta-coloured needles, which do not melt below  $251^\circ$ :

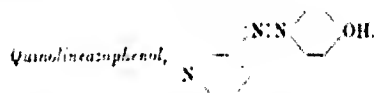
0.2346 gave 0.1474  $\text{AgCl}$ .  $\text{Cl}=19.4$ .

$\text{C}_{10}\text{H}_{11}\text{ON}_4 \cdot 2\text{HCl}$  requires  $\text{Cl}=19.0$  per cent.

*Trihydrochloride*—0.1742 absorbed 0.0678  $\text{HCl}$ . Increase = 39.0.

$\text{C}_{10}\text{H}_{11}\text{ON}_4$  requires increase = 36.5 per cent.

This substance was a purple black powder.



Prepared from diazotised 5-aminoquinoline and an alkaline solution of phenol. A deep magenta-coloured solution resulted, but no salt deposited. The liquid was acidified with acetic acid; the brownish-yellow precipitate formed was collected, washed with water and a little hot alcohol. It crystallised from alcohol in light brown, microcrystalline needles, melting at  $274^\circ$ . The compound dissolves in ordinary organic solvents, but is difficult to obtain in crystals of fair size, resembling hydroxazobenzene in this respect.

0.1366 gave 0.3602  $\text{CO}_2$  and 0.0600  $\text{H}_2\text{O}$ .  $\text{C}=71.9$ ;  $\text{H}=4.9$ .

0.1441 " 21.1 c.c.  $\text{N}_2$  at  $22^\circ$  and 764 mm.  $\text{N}=17.2$ .

$\text{C}_{17}\text{H}_{11}\text{ON}_2$  requires  $\text{C}=72.3$ ;  $\text{H}=4.4$ ;  $\text{N}=16.9$  per cent.

The substance is readily acetylated by boiling for a few hours with an equal weight of anhydrous sodium acetate and 15 parts of acetic anhydride. The acetate separates from 50 per cent. alcohol in slender, light brown plates, melting at  $192$ – $193^\circ$ .

As the crystallised material retained water, it was dried at  $100^\circ$  before analysis:

0.1108 gave 0.2832  $\text{CO}_2$  and 0.0472  $\text{H}_2\text{O}$ .  $\text{C}=69.7$ ;  $\text{H}=4.7$ .

0.1236 " 15.6 c.c.  $\text{N}_2$  at  $19^\circ$  and 759 mm.  $\text{N}=14.65$ .

$\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}_2$  requires  $\text{C}=70.1$ ;  $\text{H}=4.5$ ;  $\text{N}=14.4$  per cent.

*Quinolineazophenyl acetate* is insoluble in cold sodium hydroxide solution, but gradually dissolves on warming, giving the magenta-coloured solution of quinolineazophenol.

*Quinolinezaphenol* reacts with sodium ethoxide and ethyl ether in boiling alcoholic solution, and yields the ethyl ether. A small proportion of the substance reacts with ethyl iodide readily to form an ethiodide. The alcoholic solution of the ethyl ether was diluted with much water, and the brown precipitate collected, washed with water, and dried on a porous tile. The dried mass was extracted with hot alcohol, leaving an almost black residue, which was tarfy, and was not further examined. The alcoholic extract was diluted with an equal quantity of water, cooled, filtered, and allowed to crystallise. Long, light brown needles, melting at  $126^{\circ}$ , separated, the crystals giving a faint test for halogens:

0.1384 gave 18.9 c.c.  $N_2$  at  $21^{\circ}$  and 752 mm. N = 15.6.

$C_{12}H_{11}ON_2$  requires N = 15.2 per cent.

*Quinolinezaphenolate* dissolves in alcohol with a yellow colour; it is insoluble in sodium hydroxide solution, but with dilute or concentrated acids produces similar colour changes to the parent substance. This compound, like the acetate, retains a little water, which can only be driven off by prolonged drying at  $100^{\circ}$ .

*Quinolinezaphenol hydrochloride* was prepared by evaporation with concentrated hydrochloric acid; it does not melt below  $281^{\circ}$ :

0.1882 gave 0.0932 AgCl. Cl = 12.2.

$C_{12}H_{11}ON_2.HCl$  requires Cl = 12.4 per cent.

The *dihydrochloride* was prepared by passing hydrogen chloride over the powdered material moistened with a little chloroform; it consists of a dark red powder.

0.1902 gained 0.0565 HCl. Increase = 29.8.

$C_{12}H_{11}ON_2$  requires increase = 29.3 per cent.

This salt loses its hydrogen chloride very slowly as compared with the dihydrochloride of benzeneazohydroxyquinoline, two or three days' exposure to moist air resulting in the same loss as occurs with the latter compound in half an hour, namely, one molecule of hydrogen chloride.

#### *Ethoxyquinolinezaphenol.*

For this preparation, 8-ethoxy-5-aminoquinoline was required, and was prepared by Vix's method (*J. pr. Chem.*, 1892, [ii], **45**, 530). The diazotisation was troublesome, as frothing occurred to a slight extent, but by rapid diazotisation and filtration into the alkaline solution of phenol a deep magenta solution resulted, which, on dilution with acetic acid, gave a yellowish brown precipitate, which was washed and dried. Repeated crystallisation from alcohol

furnished light brown, microcrystalline prisms, melting at 256°, soluble in organic solvents other than benzene and ether:

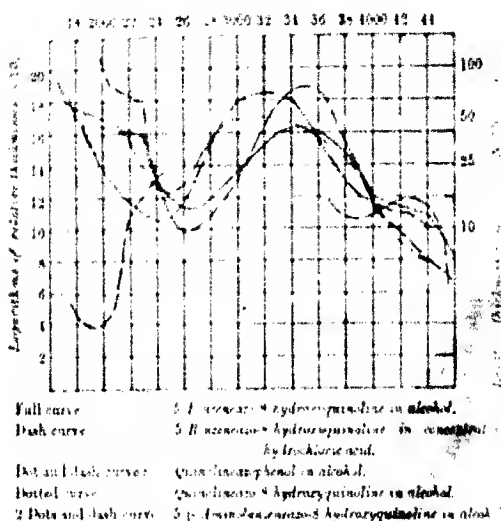
0.1206 gave 0.3324 CO<sub>2</sub> and 0.0612 H<sub>2</sub>O. C=69.4; H=5.2.

0.1128 " 14.1 cc. N<sub>2</sub> at 21° and 760 mm. N=14.4.

C<sub>17</sub>H<sub>13</sub>O<sub>3</sub>N<sub>3</sub> requires C=69.6; H=5.1; N=14.3 per cent.

Sufficient of the substance was not available to prepare a quantity of the acetate, but when acetylated in the usual way, sandy powder resulted, which crystallised from alcohol in mirror plates, melting at 143°, and did not dissolve in cold sodium

*Quinoline frequencies.*



hydroxide, but gave a deep magenta solution after heating for few minutes.

The changes in the colour of the solutions of the foregoing compounds under the action of strong mineral acids due to the formation of quinonoid salts is strikingly shown by all these substances. In alcoholic solution all of them, on the addition of little dilute hydrochloric acid, produce a yellow or, at most, a orange-coloured solution. Concentrated hydrochloric acid gives colours varying from deep red with *p*-nitrobenzeneazohydroxyquinoline to deep violet in the case of benzeneazohydroxyquinoline. Concentrated sulphuric acid gives varying shades of magenta to

purple, but with *o*-naphthaleneazohydroxyquinoline a deep blue solution was obtained. Sodium hydroxide added to the alcoholic solutions produces reddish yellow or red solutions, except with *p*-nitrobenzeneazohydroxyquinoline, which becomes violet. This behaviour towards concentrated acids, with the resulting formation of osonium salts is entirely in accord with the supposition "that a decrease in the principal vibration frequency of an azo-compound accompanies an increase in the length of chain of conjugated double linkages" (Hewitt and Mitchell, *Trans.*, 1907, **91**, 1251, Hewitt and Paley, *Trans.*, 1909, **53**, 1395). The curves of the absorption spectra (see figure) are of particular interest, inasmuch as they show that the heads of the bands are in practically the same position as was observed by Hewitt and Thomas (*Trans.*, 1907, **95**, 1297) in the case of aminobenzeneazophenol and dimethyl aminobenzeneazophenol, and are such as are given by hydroxyazo-compounds. The reaction of the dihydrochloride of benzeneazohydroxyquinoline in concentrated hydrochloric acid could not be examined in greater thickness than those shown because of the intense colour, hence it was not possible to furnish a complete curve, but the two curves shown are obviously part of one curve. Benzeneazohydroxyquinoline and quinolineazophenol give curves which differ only in the somewhat greater persistency of the band in the latter; whilst the band of quinolineazohydroxyquinoline is least persistent of all, but does not differ from the other curves to such an extent as to indicate an alteration in the configuration of the molecule.

It has been found troublesome to diazotise *N*-aminoquinoline satisfactorily, so that rather poor yields of the hydroxyazo-derivatives of this substance have been obtained, but these can be acetylated fairly readily, and the work is still proceeding. As regards the azo-derivatives of *p*-hydroxyquinoline, no attempt to acetylate by other than the usual methods was made, it being considered sufficient for comparison with the quinolineazophenols to attempt the acetylation by the ordinary methods.

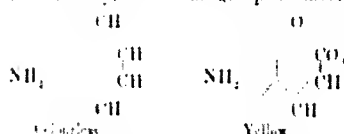
For LONDON CHEMIST

### CXXIII.—The Colour and Constitution of the Amino-coumarins.

By ARTHUR CLAYTON, B.Sc., A.R.C.S.

THE introduction of an amino-group into the molecule of a colourless substance does not generally cause the production of colour, but a peculiar exception is met with in the case of 6-amino-coumarin, which possesses a deep yellow colour, although coumarin itself is colourless. The cause of the yellow colour was investigated by Morgan and Micklethwait (Trans., 1904, 85, 1239), who showed that the colour was not affected by the substitution of methyl for one or both amino-hydrogen atoms, but was destroyed by acylation or by the formation of a quaternary salt. These investigators concluded that the cause of the colour lies in some relation between the amino-nitrogen atom and the unsaturated  $\cdot\text{O}\cdot\text{CO}\cdot$  group present in the lactonic ring, this conclusion being supported by the amino-group occupying a para position with respect to the lactonic oxygen. The author of the present communication has examined a number of amino-derivatives of coumarin and its homologues with the view of obtaining further insight into the cause of the yellow colour.

Since *β*-naphthylamine is colourless and the only difference between the formulae of this substance and 6-amino-coumarin is the substitution of the  $\cdot\text{O}\cdot\text{CO}\cdot$  group in the latter compound for the  $\cdot\text{CH}\cdot\text{CH}\cdot$  group present in the former (see formulae), it follows that the group  $\cdot\text{O}\cdot\text{CO}\cdot$  is directly involved in the production of the colour. Similarly, the amino-group is involved, because



coumarin is colourless. It has been shown by Morgan and Micklethwait (*loc. cit.*) that a mobile hydrogen atom in the amino-group does not give rise to the colour, as 6-dimethylaminocoumarin is yellow. The remaining factors possibly involved are:

1. The position in the benzenoid ring occupied by the amino-group.
2. The presence of a mobile hydrogen atom in the benzenoid ring.
3. The presence of a mobile hydrogen atom in the lactonic ring.
4. A direct connection between the  $\cdot\text{O}\cdot\text{CO}\cdot$  and amino-groups, depending on or independent of their relative positions.

(1) 5-Amino 6, 7-dimethylcoumarin, 6-amino-7-methylcoumarin,

7-amino-5:6:8-trimethylcoumarin, 8-aminocoumarin, and 5:8-di-amino-6:7-dimethylcoumarin were prepared by reducing the corresponding colourless nitro-compounds, and were in each case found to be yellow. As the above compounds contain the amino-group in each possible position in the benzenoid ring, the production of colour does not depend on the position occupied by the amino-group.

(2) Since 7-amino-5:6:8-trimethylcoumarin is yellow, and in this compound the benzenoid ring is completely substituted, the presence of a mobile hydrogen atom in the benzenoid ring is not involved in the colour formation.

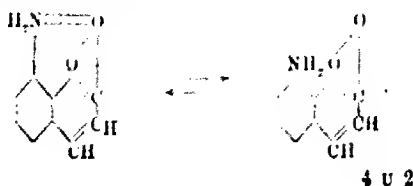
(3) 6-Amino-4:7-dimethylcoumarin, 5-amino-4:6:7-trimethylcoumarin, 5:7-diamino-4:6:8-trimethylcoumarin, and 6-amino-3:4:7-trimethylcoumarin were prepared, and all found to be yellow, hence the presence of a mobile hydrogen atom in the lactonic ring is not necessary for the production of the colour.

(4) The formation of the yellow colour appears from the above observations to be consequent on some direct connexion between the  $\cdot\text{O}\cdot\text{CO}\cdot$  and amino groups, and the results obtained in (1) show this connexion to be independent of the relative position of these groups.

Coumarin and its derivatives exhibit additive properties due to the unsaturation of the  $\cdot\text{O}\cdot\text{CO}\cdot$  group (Williamson, *Journ. Chem. Soc.*, 1875, **28**, 590; Morgan and Micklethwait, *Trans.*, 1906, **89**, 863; Clayton, *Trans.*, 1908, **93**, 524), which possesses an amphoteric nature. There is, however, a much greater tendency to combine with basic substances than with acids, so the residual affinities of the  $\cdot\text{O}\cdot\text{CO}\cdot$  group may be considered to be of a weakly acid nature.

In the case of the aminocoumarins, these acid affinities would doubtless find partial satisfaction in the extra affinities available in the aminic nitrogen atom, but owing to the weakness of the union which would exist between the  $\cdot\text{O}\cdot\text{CO}\cdot$  and amino groups, it is highly probable that the bonds uniting them would be continually broken and re-formed during intermolecular motions.

If the correct formula for coumarin is that suggested by Morgan and Micklethwait (*Trans.*, 1906, **89**, 863), the aminocoumarins may be undergoing the vibratory change indicated in the subjoined formulae for 8-aminocoumarin.



The author considers it possible that these vibrations may generate the yellow colour, and it is worthy of note that in the case of 3-aminocoumarin, where, owing to the proximity of the nitrogen and oxygen atoms concerned, the rupture of the bond would be less easily effected, the yellow colour is much less marked than in the other aminoderivatives.

The following facts support the view expressed by the above formulae:

(i) The above observation (p. 1350), that the colour vanishes when the supplementary valencies of the nitrogen atom are involved by the formation of a quaternary salt, and when the basicity of the amino-group is destroyed by acylation.

(ii) The fact that the hydrochlorides of all the aminocoumarins examined by the author are colourless.

(iii) The remarkable stability of the amino- and diamino-coumarins both in the solid state and in solution.

#### EXPERIMENTAL

*8-Aminocoumarin.* 8-Nitrocoumarin (1 gram) was suspended in boiling dilute acetic acid (100 c.c.), and gradually treated with iron filings (1 gram), after which the mixture was boiled for fifteen minutes, and filtered. The nitrate yielded crystals, which, after re-crystallisation from alcohol, formed pale yellow prisms, melting at  $115-116^{\circ}$ .

0.1987 gave 0.4818  $\text{CO}_2$  and 0.6817  $\text{H}_2\text{O}$ .  $\text{C}=66.81$ ;  $\text{H}=4.57$ .

0.1023 " 7.5 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 756 mm.  $\text{N}=8.34$ .

$\text{C}_9\text{H}_8\text{O}_2\text{N}$  requires  $\text{C}=67.08$ ;  $\text{H}=4.35$ ;  $\text{N}=8.70$  per cent.

*6-Nitro-7-methylcoumarin.* A mixture of 6-nitro-7-methylcoumarin (1 gram) and 5 per cent. acetic acid (100 c.c.) was heated to boiling and gradually treated with iron filings (1 gram), after which the liquid was boiled for fifteen minutes, then cooled and filtered. The residue was extracted with alcohol and crystallised from the same solvent, when yellow needles, melting at  $200-201^{\circ}$ , were obtained.

0.1423 gave 0.518  $\text{CO}_2$  and 0.0729  $\text{H}_2\text{O}$ .  $\text{C}=68.37$ ;  $\text{H}=5.32$ .

0.1216 " 5.7 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 756 mm.  $\text{N}=8.14$ .

$\text{C}_{10}\text{H}_9\text{O}_2\text{N}$  requires  $\text{C}=68.57$ ;  $\text{H}=5.14$ ;  $\text{N}=8.00$  per cent.

6-Amino-4,7-dimethylcoumarin was prepared from 6-nitro-4,7-dimethylcoumarin in the manner described in the preceding experiment. The product, however, was extracted with glacial acetic acid, and crystallised from this solvent in yellow needles, melting at  $203-205^{\circ}$ .

0.1781 gave 0.4540  $\text{CO}_2$  and 0.0941  $\text{H}_2\text{O}$ .  $\text{C} = 69.52$ ;  $\text{H} = 5.87$ .

0.1816 .. 12.0 c.c.  $\text{N}_2$  at  $20^\circ$  and 756 mm.  $\text{N} = 7.52$ .

$\text{C}_{11}\text{H}_9\text{O}_2\text{N}$  requires  $\text{C} = 69.84$ ;  $\text{H} = 5.82$ ;  $\text{N} = 7.41$  per cent.

5.4 Amino-6:7-dimethylcoumarin. 5-Nitro-6:7-dimethylcoumarin (1 gram) and dilute acetic acid (80 c.c.) were boiled together, and gradually treated with iron filings (0.8 gram), after which the mixture was heated for one hour. The cooled liquid was filtered and the residue extracted with alcohol, from which solvent yellow needles, melting at  $142^\circ$ , were obtained.

0.1630 gave 0.4148  $\text{CO}_2$  and 0.0871  $\text{H}_2\text{O}$ .  $\text{C} = 69.58$ ;  $\text{H} = 5.94$ .

0.1590 .. 10.7 c.c.  $\text{N}_2$  at  $21^\circ$  and 752 mm.  $\text{N} = 7.54$ .

$\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}$  requires  $\text{C} = 69.84$ ;  $\text{H} = 5.82$ ;  $\text{N} = 7.41$  per cent.

7. Amino-5:6:8-trimethylcoumarin. 7-Nitro-5:6:8-trimethylcoumarin (5 grams) was mixed with dilute acetic acid (100 c.c.) and heated to boiling, when iron filings (5 grams) were gradually added, the mixture finally being boiled for one hour. The cooled liquid was filtered, and the residue repeatedly extracted with alcohol, in which solvent the product is somewhat sparingly soluble. Recrystallisation from glacial acetic acid yielded yellow needles, melting at  $220^\circ$ – $221^\circ$ . The solution in alcohol or acetone exhibits a strong blue fluorescence, which does not appear in the solutions in benzene, toluene, or acetic acid.

0.1331 gave 0.3458  $\text{CO}_2$  and 0.0782  $\text{H}_2\text{O}$ .  $\text{C} = 70.86$ ;  $\text{H} = 6.60$ .

0.1341 .. 7.9 c.c.  $\text{N}_2$  at  $20^\circ$  and 750 mm.  $\text{N} = 6.70$ .

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C} = 70.94$ ;  $\text{H} = 6.40$ ;  $\text{N} = 6.90$  per cent.

6. Amino-4:6:7-trimethylcoumarin. 6-Nitro-4:6:7-trimethylcoumarin (2 grams) and dilute acetic acid (40 c.c.) were boiled together and treated with iron filings (2 grams), after which the mixture was boiled for one hour. The cooled liquid was filtered and the residue extracted with alcohol, from which solvent 75 per cent. of the theoretical quantity of yellow needles, melting at  $231^\circ$ – $233^\circ$ , was obtained. The substance is rather sparingly soluble in alcohol.

0.1812 gave 0.4620  $\text{CO}_2$  and 0.1047  $\text{H}_2\text{O}$ .  $\text{C} = 70.71$ ;  $\text{H} = 6.42$ .

0.1851 .. 11.3 c.c.  $\text{N}_2$  at  $20^\circ$  and 750 mm.  $\text{N} = 6.89$ .

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C} = 70.94$ ;  $\text{H} = 6.40$ ;  $\text{N} = 6.90$  per cent.

6-Nitro-3:4:7-trimethylcoumarin.—A solution of 3:4:7-trimethylcoumarin (2.3 grams) in concentrated sulphuric acid (12 c.c.) was slowly treated at  $0^\circ$  with a mixture of nitric acid (D 1.4) (1 c.c.) and concentrated sulphuric acid (3 c.c.), after which the liquid was kept at the ordinary temperature for thirty minutes, and then poured on crushed ice. The product crystallised from glacial acetic acid in colourless needles, melting at  $169^\circ$ – $170^\circ$ .



# 1254 COLOUR AND CONSTITUTION OF THE AMINO-COUMARINS.

0.1994 gave 0.4515  $\text{CO}_2$  and 0.0832  $\text{H}_2\text{O}$ .  $\text{C} = 61.76$ ;  $\text{H} = 4.64$ .

0.1514 " 7.9 c.c.  $\text{N}_2$  at  $20^\circ$  and 756 mm.  $\text{N} = 5.93$ .

$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}$  requires  $\text{C} = 61.80$ ;  $\text{H} = 4.72$ ;  $\text{N} = 6.01$  per cent.

5. *Isomer 3: 4: 7-trimethylcoumarin*. — 6-Nitro-3: 4: 7-trimethylcoumarin was reduced with iron filings and dilute acetic acid in the usual way, the liquid being boiled for twenty minutes after the addition of the iron. The cooled mixture was filtered, and the residue extracted with alcohol from which solvent the product crystallised in yellow needles, melting at  $206^\circ - 207^\circ$ . The alcoholic solution exhibits a brilliant green fluorescence.

0.1469 gave 0.379  $\text{CO}_2$  and 0.0020  $\text{H}_2\text{O}$ .  $\text{C} = 70.70$ ;  $\text{H} = 6.28$ .

0.1017 " 6.7 c.c.  $\text{N}_2$  at  $20^\circ$  and 756 mm.  $\text{N} = 7.32$ .

$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}$  requires  $\text{C} = 70.94$ ;  $\text{H} = 6.40$ ;  $\text{N} = 6.90$  per cent.

5. 4. *Isomer 6: 7-dimethylcoumarin*. — 5: 8-Dinitro-6: 7-dimethylcoumarin (2 grams) was heated to  $100^\circ$  with dilute acetic acid and gradually treated with iron filings (5 grams), the mixture being subsequently boiled for twenty minutes, then cooled and filtered. The residue was extracted with alcohol, from which solvent yellow needles, melting at  $219^\circ - 222^\circ$ , were obtained.

0.1339 gave 0.360 c.c.  $\text{N}_2$  at  $20^\circ$  and 762 mm.  $\text{N} = 13.79$ .

$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{N} = 13.73$  per cent.

5. 7. *Isomer 4: 6: 8-trimethylcoumarin*. — 5: 7-Dinitro-4: 6: 8-trimethylcoumarin was reduced with iron filings and acetic acid as in the preceding experiment. The product separated from alcohol in fine yellow needles, melting at  $218^\circ - 220^\circ$ . There was no tendency in this or the preceding experiment to form the nitro-amine.

0.1493 gave 0.2381  $\text{CO}_2$  and 0.0781  $\text{H}_2\text{O}$ .  $\text{C} = 65.72$ ;  $\text{H} = 6.18$ .

0.1093 " 1.0 c.c.  $\text{N}_2$  at  $18^\circ$  and 734 mm.  $\text{N} = 12.55$ .

$\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2$  requires  $\text{C} = 66.05$ ;  $\text{H} = 6.42$ ;  $\text{N} = 12.84$  per cent.

The author desires to express his thanks to the Chemical Society for a grant which has in part defrayed the expense incurred during this investigation.

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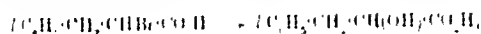
CXXIV.—*Experiments on the Walden Inversion. Part V. The Interconversion of the Optically Active  $\alpha$ -Hydroxy- $\beta$ -phenylpropionic Acids.*

By ALAN MCKENZIE and HENRY WHEAT

THE  $\beta$ -hydroxy  $\beta$ -phenylpropionic acids (this vol., p. 121) and the isomeric phenylmethylglycolic acids (this vol., p. 1016) have already been investigated with reference to the Walden inversion.

In the present communication the resolution of another of the racemic racemic "phenyl-lactic" acid, namely  $\alpha$ -hydroxy  $\beta$ -phenylpropionic acid,  $C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot COOH$ , into its optically active components is described. An aqueous solution of this acid was neutralized by morphine, and the resolution proceeded with the same ease as in the case of the  $\beta$ -hydroxy acid *discussed*, the morphine salt being much more sparingly soluble in water than the morphine salt. The resulting *d*-acid melts at  $124-125^\circ$ , whereas the *l*-acid melts at  $97-98^\circ$ . The value for the specific rotation,  $[\alpha]_D^{25} = +18.5^\circ$  for  $c = 3.5322$  in ethylalcoholic solution, is nearly identical with that obtained for the  $\beta$ -hydroxy acid under similar conditions. The *d*-acid was readily isolated from the filtrate, from which the morphine salt had separated.

The preparation of the optically active  $\alpha$ -bromo  $\beta$ -phenylpropionic acids from the inactive bromo acid has been described by E. Fischer and Carl (Ber., 1906, 39, 3906). We find that the displacement of bromine by the hydroxy group in these acids takes place very much more slowly than in any other case of halogen displacement described in this series of papers, and it is not accompanied by a change of sign of rotation. Since it is immaterial whether the displacement is effected by water, by aqueous sodium hydroxide, or by silver oxide and water, the action



appears to be a normal one.

The action of phosphorus pentachloride on the active hydroxy-acids was next examined. The *d*-acid gave a dextrorotatory  $\alpha$ -chloro acid chloride, the phosphorus pentachloride, as is always the case when it acts on an optically active acid, causing a considerable amount of racemisation. When the acid chloride was heated with sodium carbonate and water, a change of sign was found to have occurred; a levorotatory product was obtained, from which a specimen of the pure *l*-hydroxy acid was isolated. The behaviour

of the *l*-hydroxy-acid towards phosphorus pentachloride was similar. The following changes have been carried out:



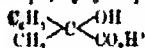
By  $CaCl_2$  and water



By  $CaCl_2$  and water

This is the first example recorded where phosphorus pentachloride appears to act abnormally.

The isomeric acids,



thus differ from one another in behaviour from the point of view of the Walden inversion.

Since phosphorus pentachloride has been found to be an agent capable of causing a transformation such as the above, and since the action of thionyl chloride on the active phenylmethylglycolic acids also proceeded in a somewhat unexpected manner (*loc. cit.*: the comparison of the action of these two chlorides on a number of active hydroxy-acids and their esters has been rendered necessary. This subject is at present under investigation.

#### EXPERIMENTAL.

##### *Resolution of $\alpha$ -Hydroxy- $\beta$ -phenylpropionic Acid.*

*r*- $\alpha$ -Hydroxy- $\beta$ -phenylpropionic acid was prepared from benzyl bromomalonate (Conrad, *Annalen*, 1880, 204, 174) by converting it into  $\alpha$ -bromo- $\beta$ -phenylpropionic ( $\alpha$ -bromohydrocinnamic) acid, and then displacing the bromine in the latter acid by the hydroxy-group (E. Fischer, *Ber.*, 1904, 37, 3062; E. Fischer and Carl, *loc. cit.*; E. Fischer and Zemlén, *Ber.*, 1909, 42, 4878).

14.7 Grams of the *r*-acid (1 mol.) were dissolved in 300 c.c. of water at about 90°, and shaken with 26.5 grams of powdered morphine (1 mol.) for a few minutes until the alkaloid had dissolved. After a night at about 8°, 24 grams of glassy crystals had separated. After crystallisation from water, 18 grams of salt were obtained, from which the acid was isolated by acidification with mineral acid and extraction with ether. The resulting acid was crystallised once from water (50 c.c.), and 4.2 grams of the pure *d*-acid were obtained.

*d*- $\alpha$ -Hydroxy- $\beta$ -phenylpropionic acid,  $C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot CO_2H$ , dissolves readily in cold methyl alcohol, ethyl alcohol, or acetone. It is readily soluble in hot water or benzene, and, on cooling,

needles, melting at 134—135°. It melts at 134—135°.

0.1309 gave 0.3176 CO<sub>2</sub> and 0.0716 H<sub>2</sub>O. C=64.8; H=6.2.

C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> requires C=65.0; H=6.1 per cent.

Its rotation was determined in ethyl-alcoholic solution:

$$l=4, c=2.5332, \alpha_D^{25} + 2.41^\circ, [\alpha]_D^{25} + 18.5^\circ.$$

Its melting point and its specific rotation in ethyl-alcoholic solution did not change after it had been recrystallized several times from water.

Its rotation was also determined in aqueous solution:

$$l=4, c=2.5622, \alpha_D^{25} + 2.34^\circ, [\alpha]_D^{25} + 22.8^\circ.$$

The enantiomorphously related acid was obtained from the mother liquor, from which the morphine *d*-salt had separated. The crude acid (7.5 grams) was crystallized from water (70 c.c.); the yield of the *l*-acid was 4 grams. It was obvious that the difference in solubility in water between the active and the inactive isomerides was such as to render the isolation of the pure active acid from a mixture of active and inactive acids a simple operation in the case mentioned.

*l*-Hydroxy- $\beta$ -phenylpropionic acid, like the *d*-acid, melts at 134—135°:

0.1309 gave 0.3124 CO<sub>2</sub> and 0.0716 H<sub>2</sub>O. C=65.1; H=6.1.

C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> requires C=65.0; H=6.1 per cent.

A determination of its specific rotation in ethyl-alcoholic solution gave the result:

$$l=4, c=2.9332, \alpha_D^{25} - 2.19^\circ, [\alpha]_D^{25} - 18.7^\circ.$$

In another experiment, where 18 grams of the *c*-acid, 410 c.c. of water, and 33 grams of morphine were employed, crystallization was induced by the addition of a nucleus of the morphine *d*-salt. From the 22.5 grams of salt which separated after a night at about 9°, 6.1 grams of nearly pure *d*-acid were obtained, with  $[\alpha]_D + 17.8^\circ$  for  $c=6.748$  in ethyl-alcoholic solution. After one crystallization from water, the acid was obtained with the rotation quoted above. The filtrate, from which the morphine *d*-salt had been removed, gave 6.1 grams of acid, which had  $[\alpha]_D - 18.8^\circ$  for  $c=6.95$  in ethyl-alcoholic solution, and, after one crystallization from water, the acid was pure.

The resolution of the inactive acid is accordingly very easily carried out; possibly the addition of a nucleus of the morphine *d*-salt is of service.

Fischer and Carl (*loc. cit.*) employed both lysine and quinine for the resolution of inactive  $\alpha$ -bromo- $\beta$ -phenylpropionic acid. The most active product obtained by them had  $[\alpha]_D - 8.3^\circ$ , but, since it was frozen out from a mixture of *s*- and *l*-acids at  $0^\circ$ , it contained, as Fischer and Carl point out, some of the *r*-form. The various specimens of acids used in the following experiments were prepared by the quinine method, and were also not homogeneous.

*Action of Water.*—The bromo-acid used had  $[\alpha]_D - 5.1^\circ$  in ethyl-alcoholic solution. A solution of 2.5 grams in 200 c.c. of water was heated at  $100^\circ$  for about fifty hours, but, even after this treatment, the displacement of the bromine by the hydroxy-group was not complete. The resulting acid was crystallised once from benzene, in which the bromo-acid is readily soluble; the hydroxy-acid obtained was levorotatory, having  $[\alpha]_D - 5.6^\circ$  in ethyl-alcoholic solution.

Similarly, a dextrorotatory bromo-acid, with  $[\alpha]_D + 7.4^\circ$  in ethyl-alcoholic solution, was heated with water in an open dish for about thirty hours, the water being renewed from time to time. The hydroxy-acid, obtained as before, had  $[\alpha]_D + 12.7^\circ$  in ethyl-alcoholic solution.

*Action of Calcium Carbonate and Water.*—The dextrorotatory bromo-acid, as used in the preceding experiment, was boiled for several hours with water and calcium carbonate. The resulting hydroxy-acid, after one crystallisation from water, was free from bromine, and had  $[\alpha]_D + 15.8^\circ$  in ethyl-alcoholic solution.

*Action of Aqueous Sodium Hydroxide.*—A solution of 1.1 grams of bromo-acid, with  $[\alpha]_D + 7.4^\circ$  in 110 c.c. of aqueous sodium hydroxide (0.1047*N*), was heated for four hours at about  $100^\circ$ . The resulting acid was crystallised from benzene, and the practically pure *d*-hydroxy-acid obtained.

*Action of Mercuric Oxide and Water.*—Here again a dextrorotatory bromo-acid gave the *d*-hydroxy-acid.

*Action of Water on Silver  $\alpha$ -Bromo- $\beta$ -phenylpropionate.*—The dextrorotatory bromo-acid, with  $[\alpha]_D + 5.2^\circ$  in ethyl-alcoholic solution, was converted into silver salt, which was heated with an excess of water for nine hours at  $100^\circ$ . The resulting acid, after one crystallisation from benzene, had  $[\alpha]_D + 13.4^\circ$  in ethyl-alcoholic solution.

When the dextrorotatory bromo-acid was heated with silver oxide and water at  $100^\circ$ , partial oxidation took place, but the resulting hydroxy-acid was dextrorotatory.

### Preparation of the *O*-hydroxy-acid

5.2 grams of *l*-phenylpropionic acid (5.7 grams) was mixed with phosphorus pentachloride (14 grams). The evolution of hydrogen chloride began at the ordinary temperature. The mixture was inserted with a tube condenser, and gradually heated to 140° during an interval of three hours. After one hour at 140–145°, the action was not quite complete. The phosphoryl chloride was accordingly distilled off, and the temperature maintained at 3–200° during two hours. No phosphorus pentachloride separated on cooling. The product was distilled under diminished pressure, and an oil, boiling mainly at 115–117°/9 mm., was collected. This was diluted slightly with ether, and examined polarimetrically in a 50 mm. tube; it had  $\alpha_D + 4.0^\circ$ . The oil was then boiled with a large excess of calcium carbonate and water for eight hours. The acid was extracted and found to be *laevorotatory*, giving the value  $[\alpha]_D - 11.3^\circ$  in ethylalcoholic solution. After one crystallisation from benzene, the product melted at 13–125°, and had  $[\alpha]_D - 16.3^\circ$  in ethylalcoholic solution. It was then crystallised from water. The resulting acid melted at 14–125°, and had  $[\alpha]_D - 18.0^\circ$  in ethylalcoholic solution. The identity of this acid with the pure *l*-hydroxy-acid was further shown by a determination of the melting point of a mixture of the two.

The *l*-hydroxy-acid was converted into the *d*-hydroxy-acid in a similar manner.

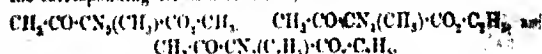
A further experiment was carried out with the *d*-hydroxy-acid under conditions somewhat different from the above. The acid (5.2 grams) was heated with phosphorus pentachloride (19.6 grams), the latter being taken in this case in excess. The temperature was gradually raised to 150° during two hours, the phosphoryl chloride then distilled off, and the temperature gradually raised to 190° during thirty minutes. The product was then added to water and treated with calcium carbonate and water as before. After removal of the excess of calcium carbonate, the filtrate (75 c.c.) was *laevorotatory*, 25 c.c. of it in a 4-dm. tube giving  $\alpha_D - 1.09^\circ$ . The acid extracted from the calcium salt had  $[\alpha]_D - 9.6^\circ$  in ethylalcoholic solution.

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CXXV.—*The Triazo-group. Part XIV. Azomides of the Acetoacetic Series.*

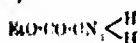
By MARTIN OSWALD FORSTER and SIDNEY HERBERT NEWMAN

As a natural sequence to the series of substituted triazomalonic esters (this vol., p. 126), we proceeded to study the corresponding derivatives of acetoacetic ester, and it may be stated at once that the result has been somewhat disappointing, on account of the subsidiary changes which take place under the conditions usually observed for the displacement of halogen by the triazo-group. For this reason it has not been possible to produce  $\alpha$ - or  $\gamma$ -triazooacetoacetic ester, and although a small quantity of  $\alpha$ -bistriazooacetoacetic ester has been isolated, the yield of this material, owing to circumstances which are explained later, is scarcely more than 5 per cent. By the interaction of methyl and ethyl  $\alpha$ -chloromethylacetoacetate and of ethyl  $\alpha$ -chloroethylacetoacetate with sodium azide, however, the corresponding triazo-derivatives,

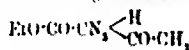


have been prepared, but it has to be noted that substitution of the azomide nucleus for chlorine in this group of esters takes place much less readily than among those of the acetic and malonic series, in consequence of this limitation, the yield of each product has been very far below that which might reasonably have been expected, especially in the case of  $\alpha$ -triazooethylacetoacetic ester.

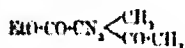
In reviewing the behaviour which characterises the azomides of the acetoacetic series, it is convenient to recall their relationship with ethyl triazooacetate by means of the following formulae:



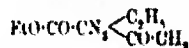
Ethyl triazooacetate.



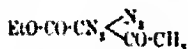
Ethyl triazooacetate  
(not isolated).



Ethyl triazomethylacetoacetate.



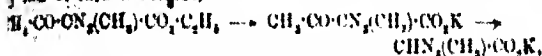
Ethyl triamethylacetoacetate.



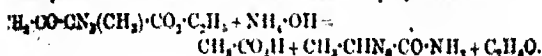
Ethyl bistriazooacetate.

From this it appears that the effect of introducing an acetyl group into the triazooacetic ester molecule corresponds with that produced by the carboxyethyl radical, the secondary character of triazomised carbon in both triazomalonic and triazooacetoacetic esters

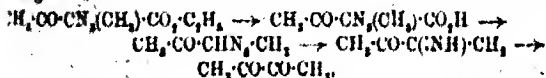
undergoing these compounds too unstable for isolation. If, however, as in the case of hydrogen in the latter substance is replaced by an  $\text{N}_3$  group, stability is restored, but the resulting esters, unlike those of the triazomalonic series, cannot be made to yield the parent acid, owing to the readiness with which disruption of the chain takes place in the direction of either ketone or acid hydrolysis. Nevertheless, the study of these compounds has furnished an illustration of the stability which characterises even a triazo-ketone when the triazotised carbon atom is tertiary. The esters in question may be regarded as substitution products of triazoacetone in which a methylenic hydrogen has been completely replaced, and therefore represent a new type; when compared with triazoacetone, isobutanone, phenacylazoinide, and a triazocampbor, the dependence of such triazo-ketones upon hydrogen for the transformation which characterises their behaviour towards alkali hydride is clearly indicated. As noticed already in the substituted triazomalonic series, the liberation of nitrogen by the action of potassium hydroxide is only consequent on hydrolysis followed by loss of carbon dioxide,



substituted  $\alpha$ -triazooacetic acid being formed. The action of ammonia on  $\alpha$ -triazomethylacetoacetic ester establishes this point, as the product has been identified with  $\alpha$ -triazopropionamide:



Whilst this change illustrates the result of "acid hydrolysis," the alternative decomposition of acetoacetic derivatives, namely, ketone hydrolysis, has been effected by means of hydrochloric acid, incidentally bringing to light a new reaction for triazo-ketones of the aliphatic series. On shaking  $\alpha$ -triazomethylacetoacetic ester with hydrochloric acid (D 1.2), gas is slowly liberated, crystals of ammonium chloride separate, and a clear, bright yellow solution is produced. This must be ascribed to the following change:



Because diacetyl has been recognised as the final product. The liberation of a triazo-ketone indicated by this series of reactions has not been observed before, but there seems to be no doubt that it is the proper interpretation of the appearance of diacetyl, as we find that triazoacetone itself effervesces vigorously with concen-



with hydrochloric acid, easily yielding crystals of ammonium chloride; under the same treatment triazomethyl ester is merely hydrolysed, without giving nitrogen or ammonia.

A curious point of difference between the triazo-group and a similarly situated chlorine atom follows from the action of semicarbazide on ethyl  $\alpha$ -triazomethylacetate, which is converted into the semicarbazone,  $\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CN}(\text{CH}_3)\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ ; on exposing the parent chloro-derivative to the same agent, the product was found to have lost the halogen, and as we have not met with any description of the interaction between semicarbazide and the chloro-derivatives of substituted acetoacetic esters, the matter seems to deserve further study in connexion with the influence of negative groups on the formation of semicarbazones (Rupe and Komler, *Ber.*, 1909, 42, 4715).

A general comparison between the azoimides of the acetoacetic series and those of the malonic group shows the  $\beta$ -ketonic esters to be less easily obtainable, and less stable when produced, than the dicarboxylic esters. Particularly noticeable is this in the case of  $\alpha\alpha$ -bistriazoacetoacetic ester. Whilst the specimen of bistriazo-malonic ester has remained clear and limpid during nine months in darkness,  $\alpha\alpha$ -bistriazoacetoacetic ester, within four days after distillation, deposited a mass of colourless crystals which have been identified with the substance spontaneously separating from bistriazoacetic ester (m. p. 91°). From this it is evident that the tendency to break up into acetic acid and disubstituted acetic ester,

$$\text{CH}_3\text{CO}\cdot\text{C}(\text{N}_3)_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5 + \text{H}_2\text{O} = \text{CH}_3\cdot\text{CO}_2\text{H} + \text{CH}(\text{N}_3)_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$$

is even more pronounced on the part of  $\alpha\alpha$ -bistriazoacetoacetic ester than in the case of  $\alpha\alpha$ -dichloroacetoacetic ester, which yields dichloroacetic ester with alkalis and ammonia, but is comparatively stable in absence of these agents. Furthermore, in preparing bistriazoacetoacetic ester, it was noticed that a considerable proportion of dichloroacetic ester accompanied the substance, and this circumstance, together with the rapid change undergone by the bistriazo compound, would explain the very disappointing yield of the latter material. In view of the foregoing remarks it is not surprising to find that  $\alpha\alpha$ -bistriazoacetoacetic ester, when treated with alkali hydrazide, gives rise to potassium cyanide in association with the azide, as the formation of prussic acid has been connected hitherto with only those bistriazo-compounds in which both acidic groups are attached to the same carbon atom.

# EXPERIMENTAL

## Attempts to Prepare Ethyl Triazacetate.

The interaction of  $\alpha$ -chloroacetoacetic ester and sodium azide in aqueous alcohol recalled the experiences connected with attempts to prepare triazomalonic ester (this vol., p. 130); evidence of the production of a triazo-compound was given, but the material appeared to be very easily decomposed by water, and we therefore failed to separate it from its products of change and from the unaltered chloro-ester. There does not appear to be any action when dry sodium azide is shaken with an ethereal solution of ethyl chloroacetoacetate, and the change which takes place on removing the solvent is too profound, even at moderate temperatures, to encourage any hope that the  $\alpha$ -triazacetoacetic ester might be isolated.

## Methyl $\alpha$ -Triazomethylacetoacetate, $\text{CH}_3\text{CO}\cdot\text{CN}(\text{CH}_3)\cdot\text{CO}_2\cdot\text{CH}_3$ .

The chloro-ester required for the preparation of this material does not appear to have been described.

Methyl  $\alpha$ -Chloromethylacetoacetate,  $\text{CH}_3\text{CO}\cdot\text{CCl}(\text{CH}_3)\cdot\text{CO}_2\cdot\text{CH}_3$ , was produced on adding sulphuryl chloride (34 grams) drop by drop to methyl methylacetoacetate (32 grams) at zero, the liquid being then allowed to take the temperature of the laboratory; after an interval of twelve hours it was heated one hour on the water-bath, poured into water, and extracted with ether, the solution being shaken with small quantities of water until no longer acid. The residue from the dried extract was distilled at  $75\text{--}76^\circ/13\text{ mm.}$  yielding 3½ grams:

$\text{D}_{20}^{25}$  gave  $\text{D}_{20}^{1100}\text{ AgCl. Cl} = 21.86$ .

$\text{C}_6\text{H}_8\text{O}_4\text{Cl}$  requires  $\text{Cl} = 21.54$  per cent.

The ester is a colourless liquid, having a faint odour of pepper, mint.

Preliminary experiments showed that replacement of chlorine by the triazo-group does not take place very readily in this series when the hydrogen of the methylene group is entirely substituted; merely shaking the chloro-ester with alcohol and aqueous sodium azide during twenty-four hours gave a product consisting mostly of unchanged material, although a certain proportion of the triazo-derivative was indicated by its behaviour towards potassium hydroxide, stannous chloride, and concentrated sulphuric acid; this was borne out by analysis, which showed that transformation to the extent of about 40 per cent. had taken place. The product

from methyl  $\alpha$ -chloromethylacetate, which had been shaken during twenty hours with 25 grams of sodium azide and the necessary amount of water and alcohol to form a clear solution, was separated in the usual manner and shaken during a further period of twenty hours with 20 grams of sodium azide; as it still contained chlorine and an insufficient percentage of nitrogen, it was heated under reflux during five hours with the alcoholic liquid still containing sodium azide, and finally salted out with ammonium sulphate. Distillation of the dried liquid revealed a mixture, although there was no longer any chlorine present. A specimen of the pure triazo-ester was ultimately obtained by heating 34 grams of the chloro-ester in absolute alcohol with 20 grams of sodium azide in water during thirty hours under reflux. Here it was noticed that the proportion of first runnings was considerable, but 12 grams of a less volatile fraction distilled at  $75-76^{\circ}/0.66$  mm.:

0.1208 gave 25.7 c.c.  $N_2$  at  $18^{\circ}$  and 756 mm.  $N=24.44$ .

0.1625 " 34.4 c.c.  $N_2$  "  $17^{\circ}$  " 764 mm.  $N=24.69$ .

$C_6H_8O_2N_2$  requires  $N=24.56$  per cent.

The ester is a colourless liquid without characteristic odour until warmed with water, when it develops a fragrant perfume, quite distinct from the peppermint suggested by the chloro-ester; it does not explode on a hot plate, and becomes only pale yellow during the lapse of several months if protected from light. Its sp. gr. is 1.1453 at  $21^{\circ}/21^{\circ}$ . The effervescence with stannous chloride in hydrochloric acid is vigorous, and yields two-thirds the azide nitrogen:

0.1738 gave 24.8 c.c.  $N_2$  at  $18^{\circ}$  and 763 mm.  $N=16.29$ .

$C_6H_8O_2N_2$  requires  $\frac{2}{3}N=16.37$  per cent.

Concentrated sulphuric acid also decomposes the substance, but not violently, whilst 30 per cent. aqueous potassium hydroxide effects hydrolysis at first without effervescence, although liberation of nitrogen occurs on heating the liquid, which is then found to contain only a trace of azide, without cyanide. Ferric chloride does not develop a coloration with the ester.

*Ethyl  $\alpha$ -Triazomethylacetate*,  $CH_3 \cdot CO \cdot CN \cdot (CH_2)_2 \cdot CO_2 \cdot C_2H_5$ .

The ethyl  $\alpha$ -chloromethylacetate required for the preparation of this material was obtained in the manner described by Roubieff (Annalen, 1890, 259, 254); it was distilled at  $82^{\circ}/15$  mm.

The chloro-ester (35 grams) in alcohol was heated with sodium azide (15 grams) in water during fifty to sixty hours under reflux, the product being precipitated with water and ammonium sulphate. As in the case of the methyl ester, there was a considerable pro-

portion of first runnings following the complete removal of ether and alcohol, but the continued heating had displaced all chlorine; the purified ester boiled at  $85^{\circ}/1$  mm.

0.1967 gave 39.0 c.c.  $N_2$  at  $20^{\circ}$  and 758 mm.  $N = 22.41$ .

$C_7H_{11}O_3N_3$  requires  $N = 22.70$  per cent.

The substance resembles the methyl ester in all its properties, and has a sp. gr. of 1.1070 at  $18^{\circ}/18^{\circ}$ ; it does not explode on a hot plate, and the vapour in steam, when inhaled, does not produce the throbbing effect in the head which characterises that of triazoacetic ester. There is not any development of colour with ferric chloride.

The semicarbazone,  $CH_3 \cdot C(N \cdot NH \cdot CO \cdot NH_2) \cdot CN_3 \cdot (CH_3) \cdot CO_2 \cdot C_2H_5$ .—After mixing 3 grams of the ester in a few c.c. of alcohol with an aqueous solution of semicarbazide acetate prepared from 3 grams of the hydrochloride, lustrous, transparent prisms separated in the course of a few hours; recrystallisation from benzene gave silky, snow-white needles, melting at  $122^{\circ}$  to a pale magenta liquid:

0.2334 gave 0.3390  $CO_2$  and 0.1226  $H_2O$ .  $C = 39.62$ ;  $H = 5.88$ .

0.1019 „ 31.6 c.c.  $N_2$  at  $25^{\circ}$  and 760 mm.  $N = 34.60$ .

$C_9H_{14}O_3N_4$  requires  $C = 39.67$ ;  $H = 5.78$ ;  $N = 34.71$  per cent.

The substance is freely soluble in acetone or chloroform, and dissolves readily in hot water, crystallising in long, lustrous needles on cooling; it is insoluble in boiling petroleum, and dissolves sparingly in cold benzene, but 1 gram requires only 3 c.c. of the hot solvent. Effervescence with concentrated sulphuric acid is very sluggish, but when stannous chloride is added to a suspension in dilute hydrochloric acid, nitrogen is liberated immediately, a clear solution being formed:

0.1208 gave 12.0 c.c.  $N_2$  at  $25^{\circ}$  and 760 mm.  $N = 11.34$ .

$C_9H_{14}O_3N_4$  requires  $N = 11.53$  per cent.

Aqueous 30 per cent. potassium hydroxide forms a clear, yellow solution, which becomes colourless on boiling; ammonia is thereupon liberated, and potassium azide produced.

Ethyl  $\alpha$ -Triazoethylacetoacetate,  $CH_3 \cdot CO \cdot CN_3 \cdot (C_2H_5) \cdot CO_2 \cdot C_2H_5$ .

Ethyl  $\alpha$ -chloroethylacetoacetate was first prepared by Conrad (Annalen, 1877, 186, 241) from ethylacetoacetic ester and chlorine, whilst Liebert (Annalen, 1886, 234, 187) employed phosphorus pentachloride; we used sulphuryl chloride, as recommended by Roubleff (loc. cit.) for the corresponding methyl derivative. From 50 grams of ethylacetoacetic ethyl ester and 44 grams of sulphuryl chloride, 45 grams of the chloro-ester, boiling at  $90^{\circ}/11$  mm. and  $64^{\circ}/0.83$  mm., were obtained.

The difficulty experienced in transforming the chloromethyl acetate was accentuated in the case of the ethyl derivative, and after several unsuccessful experiments it was found necessary to heat the ester in alcohol with aqueous sodium azide under reflux during upwards of one hundred hours before exchange of halogen for the triazo-group appeared to be complete. This protracted treatment naturally led to a considerable degree of subsidiary decomposition, which was indicated by the separation of a large earlier fraction when the product was distilled; from 40 grams of chloro-ester only 10 grams were collected at 84–86°/0.9 mm., although the same quantity of first runnings contained but a trace of chlorine:

O.1501 gave 28.2 c.c.  $N_2$  at 21° and 764 mm.  $N = 21.49$ .

$C_6H_{10}O_3N_3$  requires  $N = 21.11$  per cent.

The ester has a very faint odour, which becomes strong and fragrant in steam; it does not explode on a hot plate, and is quite stable when protected from light. It has a sp. gr. of 1.0536/19°. The action with concentrated sulphuric acid is very vigorous, while stannous chloride acts slowly; aqueous potassium hydroxide first hydrolyses the ester and liberates gas on heating, but does not produce either hydrazic or prussic acid. Ferric chloride is without action on the ester.

The semicarbatone,  $CH_3 \cdot C(N \cdot NH \cdot CO \cdot NH_2) \cdot CN_3 \cdot (C_2H_5) \cdot CO_2 \cdot C_2H_5$ , separated more slowly than that of the methyl derivative, and was much more readily soluble in benzene, from which it crystallised in transparent plates, retaining the solvent, and melting indefinitely at about 130° ( $N = 30.52$ ;  $C_9H_{14}O_3N_4$  requires  $N = 32.81$ ). On re-crystallisation from boiling water, the hydrocarbon was liberated, and there separated long, lustrous needles, melting at 135°:

O.1361 gave 39.0 c.c.  $N_2$  at 23° and 754 mm.  $N = 32.04$ .

$C_9H_{14}O_3N_4 + \frac{1}{2}H_2O$  requires  $N = 31.70$  per cent.

The presence of the triazo-group was demonstrated by stannous chloride, concentrated sulphuric acid, and aqueous potassium hydroxide, the last-named decomposing the substance when heated, producing a transient yellow coloration, and liberating ammonia.

#### *Acid and Ketone Hydrolysis of Ethyl $\alpha$ -Triazomethylacetoacetate.*

The production of nitrogen when the alkylacetoacetic azoimides are heated with aqueous potassium hydroxide is doubtless due to "acid hydrolysis," which should give rise to the corresponding alkyltriazacetic acid; when shaken with cold 30 per cent. aqueous potassium hydroxide, the ethyl ester of  $\alpha$ -triazomethylacetoacetic acid quickly formed a clear solution, and, after acidification, the

remains from the ethereal extract had the rancid odour of  $\alpha$ -triazopropionic acid, and did not develop colour with ferric chloride. More definite evidence that the decomposition takes this direction is furnished by the action of ammonia. Two grams of ethyl  $\alpha$ -triazomethylacetoacetate were shaken at zero with 10 c.c. of concentrated ammonia until a clear solution was formed, this being kept in a vacuum desiccator until crystals appeared; the product was recrystallised from benzene, and melted at  $80^\circ$  without depressing the melting point of triazopropionamide prepared from ethyl  $\alpha$ -triazopropionate and ammonia (Trans., 1908, 93, 673).

The course of the "ketone hydrolysis" is shown by the behaviour of  $\alpha$ -triazomethylacetoacetic ester towards concentrated hydrochloric acid. One gram was shaken at intervals with 5 c.c. of this agent, when the liquid slowly became yellow and evolved gas; after many hours, crystals of ammonium chloride separated, and on diluting with water and extracting with ether, the residue from the latter was shown to contain diacetyl by means of the test described by Sachs and Rohmer (Ber., 1902, 35, 3311). The reaction in question does not appear to be well known; but it offers a very simple and striking method of recognising the diketone, which is mixed with common benzene containing thiophen, and treated with concentrated sulphuric acid; a very intense dark green coloration is developed when diacetyl is present.

*Ethyl  $\alpha$ -Bis-triazooacetoacetate*,  $\text{CH}_3\text{CO}\cdot\text{C}(\text{N}_3)_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ .

Much time and material has been spent in attempting to isolate the bis-triazo-ester, and although a small quantity of the substance has been obtained on two occasions, it is accompanied by a mixture of more volatile compounds, of which the principal constituent is ethyl dichloroacetate, due to disruption of the dichloroacetoacetic molecule prior to double decomposition with sodium azide.

$\alpha$ -Dichloroacetoacetic ester (25 grams) in alcohol (40 c.c.) was shaken at frequent intervals during six days with 25 per cent. aqueous sodium azide (100 grams); hydrazoic acid was liberated freely, and when the residue from ether extraction was distilled under reduced pressure, a considerable proportion of a colourless, pungent liquid passed over, 5 grams boiling steadily at  $61-64^\circ/25$  mm. This did not effervesce with concentrated sulphuric acid, and was identified with ethyl dichloroacetate by conversion into the amide, which did not depress the melting point of dichloroacetamide when mixed with that substance. The residue from the initial distillation was then heated under 0.9 mm. pressure, yielding 1.2 grams at  $81-82^\circ$ , and leaving a few drops of pale brown material which became crystalline on cooling. The distillate had a more

pungent and distinctive odour than that of the triazooacetic ester described above; on one occasion the attempt to estimate nitrogen led to an explosion:

O-0459 gave 23.0 c.c.  $N_2$  at  $25^\circ$  and 766 mm.  $N=33.25$ .

$C_9H_6O_3N_4$  requires  $N=39.62$  per cent.

The ester does not develop colour with ferric chloride, even when heated, indicating that it is fairly stable. The decomposition with concentrated sulphuric acid is very violent, and brisk effervescence takes place with stannous chloride in hydrochloric acid. When shaken with 30 per cent. potassium hydroxide, the mixture becomes warm and liberates nitrogen steadily, but not in large quantity, and probably therefore the decomposition is due to preliminary "acid hydrolysis" leading to bistriazooacetic acid, in which the triazotised carbon, being secondary, loses the azomide complex very readily; the clear alkaline liquid yields a further quantity of nitrogen when heated, and contains potassium azide and cyanide.

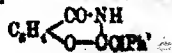
A more definite proof of transformation into bistriazooacetic ester is given by the alteration which *aa*-bistriazooacetoacetic ester undergoes with lapse of time. One c.c., preserved in darkness during six months, deposited a glassy crystal weighing 1 decigram; this melted at  $91^\circ$ , and when mixed with the similar substance deposited by bistriazooacetic ester (this vol., p. 130) melted still at that temperature. A second specimen of bistriazooacetoacetic ester changed into this crystalline compound within four days of being distilled, and it is no doubt in part due to this complete and rapid decomposition that the yield of the bistriazo-derivative is so small.

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### CXXXVI.—6-Chloro-2-phenyl-1:3-benzoxazine-4-one and Related Derivatives.

By ARTHUR WALSH TITHERLEY and ERNEST CHISLETT HUGHES

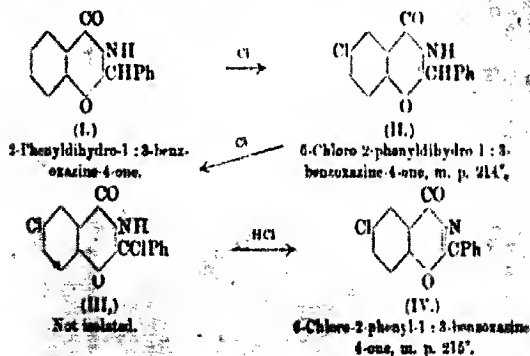
THE cyclic hydroxyoxazone derivative,  $C_9H_6\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \diagdown \quad \diagup \\ \text{O} \end{smallmatrix}\text{CPh}\cdot\text{OH}$ , intermediate in the reversible rearrangement of the two benzoylsalicyl anilides appears to be quite incapable of separate existence, and when produced by oxidation of 2-phenyldihydro-1:3-benzoxazine-4-one ("phenylbenzoxetoxazone") yields *N*-benzoylsalicylamide (Titherley, *Trans.*, 1907, 91, 1420). The object of the present investigation was to prepare the related 2-chloro-derivative,



with a view to studying its behaviour when the chlorine atom was replaced by hydroxyl, and the mode of preparation attempted was the chlorination of 2-phenyldihydro-1:3-benzoxazine-4-one (I) in the expectation that the hydrogen atom in position 2 might be replaced by chlorine. A possible alternative reaction is that of substitution in the benzene nucleus.

The chlorination was carried out under a variety of conditions, but in no circumstances could the desired 2-chloro-derivative be obtained. While the work was in progress it became evident that this derivative, if formed, would be unstable, and immediately lose hydrogen chloride. One of the authors (Titherley, this vol., p. 300) has now shown that this 2-chloro-compound is probably produced as an intermediate product in the action of hydrogen chloride on either *O*- or *N*-benzoylallylamine, but that it at once loses hydrogen chloride, yielding the unsaturated compound, 2-phenyl-1:3-benzoxazine-4-one,  $C_8H_7<\overset{(X)}{N}>\overset{O}{C}Ph$ .

An examination of the products of chlorination of the oxazone (I) under all conditions made it clear that the chlorine had substituted hydrogen in the benzene nucleus, and by working carefully it was possible to isolate two monochloro-derivatives of almost identical melting point (214–215°), the proportions of which varied with the time of chlorination. One of these, formed first, was shown to be a simple chloro-substitution derivative (II), and the other, the amount of which increased with time, was proved to be the chloro-derivative (IV) of the unsaturated cyclic compound recently described by Titherley (*loc. cit.*). It is evident that, although substitution first takes place in the benzene ring, the hydrogen atom at position 2 in the oxazone nucleus is subsequently replaced, giving the 2-chloro-derivative (III), which loses hydrogen chloride as fast as it is formed:

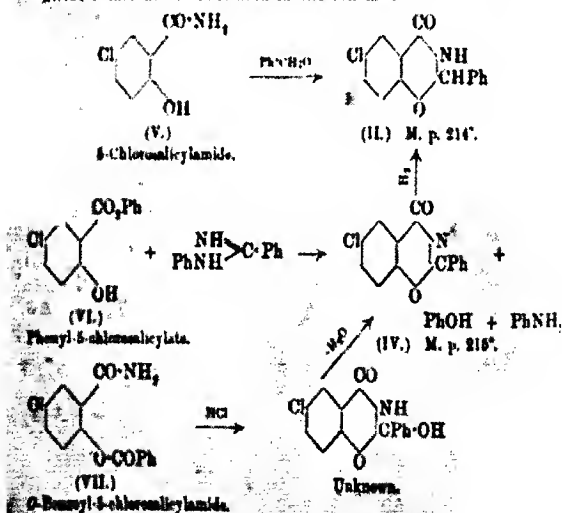




Owing to the great similarity in the physical properties of these two chloro-derivatives (II and IV), and the fact that they give practically the same figures for chlorine and nitrogen on analysis, considerable difficulty was encountered in isolating them and establishing their separate identity. Advantage was eventually taken of a marked difference in their velocities of formation in fixing the optimum conditions for the preparation of the two substances.

The position of the chlorine atom (6) in the two compounds was proved by the fact that, on alkali hydrolysis, 5-chlorosalicylamide (V) was produced; and the constitution of the compound (II) was confirmed by its independent synthesis by the condensation of 5-chlorosalicylamide and benzaldehyde (compare Titherley and Hicks, *Trans.*, 1909, 95, 915). Similarly, the constitution of the unsaturated cyclic compound (IV) was confirmed by its independent synthesis from phenyl 5-chlorosalicylate (VI) and phenylbenzamidine by a method similar to that by which 2-phenyl-1:3-benzoxazine-4-one has been recently obtained from phenyl salicylate, as well as by the internal condensation of *O*-benzoyl-5-chlorosalicylamide (VII) under the catalytic influence of hydrogen chloride, similar to that of *O*-benzoylsalicylamide (compare Titherley, this vol., p. 200). Further, the relation between the two chloro-compounds has been confirmed by the fact that the unsaturated compound (IV), on reduction, is transformed into the dihydro-derivative (II).

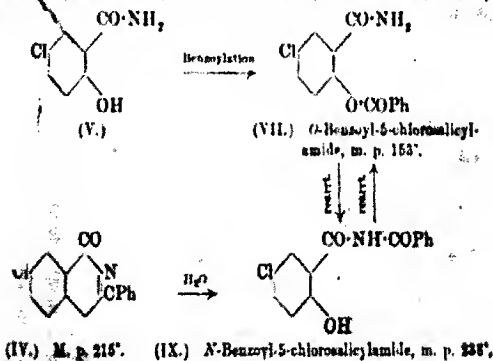
These relations are indicated in the scheme:



The two chloro-compounds (II and IV) differ strongly in their chemical properties, and whilst the dihydro-compound (II) on alkali hydrolysis at 100° yields benzaldehyde, the unsaturated ring compound (IV) yields benzoic acid. The dihydro-compound is similar throughout in its properties to its parent substance, "phenyl-benzoxetazone," and on treatment with pyridine and alkali suffers a similar ring rupture (compare Titherley, *Trans.*, 1907, 91, 1430), yielding the isomeric *syn*-benzylidene-5-chlorosalicylamide (VIII), which is even more labile than the corresponding simple *syn*-benzylidenesalicylamide (*loc. cit.*), and rearranges readily into the cyclic compound (II):



The unsaturated chloro-derivative (IV) is similar in its chemical properties to the parent substance,  $C_6H_5\text{--}\begin{smallmatrix} \text{CO} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C} \cdot \text{Ph} \end{smallmatrix}$ , but melts more than 100° higher, and is much less soluble in solvents. Moreover, it is much more stable in respect of the 1:3-oxazone ring, and whereas the parent compound is extremely sensitive to aqueous acids in the cold, the chloro-derivative (IV) is only slowly affected. On heating, however, it is easily ruptured with addition of water, giving *N*-benzoyl-5-chlorosalicylamide (IX), which has been shown to be identical with the rearrangement product (on melting) of *O*-benzoyl-5-chlorosalicylamide (VII). Conversely, the *N*-benzoyl derivative (IX) is rearranged to the *O*-benzoyl isomeride (VII) by



boiling with acetic acid, and complete identity has been established between this *O*-benzoyl derivative and the product of pyridine benzoylation of 6-chlorosalicylamide (V) at  $-15^{\circ}$ .

The rearrangement phenomena are analogous in every particular to those observed between *O*- and *N*-benzoylsalicylamides by McConnan and Titherley (Trans., 1906, 80, 1318), and the above relations are expressed in the scheme on p. 1371.

#### EXPERIMENTAL.

##### *The Action of Chlorine on 2-Phenyldihydro-1:3-benzoxazine-4-one*

(a) *Without Solvent*.—A number of experiments were carried out without solvent at  $110^{\circ}$  and higher temperatures, both in bright daylight and in the dark. Illumination did not sensibly affect the course of the reaction. During the passage of the chlorine, the solid in the flask slowly melted, and after about an hour a yellow semi-solid mass resulted, which, after cooling, on treatment with cold benzene left a white, crystalline solid. The latter consisted of a mixture in varying proportions of 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one and 6-chloro-2-phenyl-1:3-benzoxazine-4-one which were never completely separated by recrystallization. The benzene filtrate, on keeping, deposited a solid, which gave a yellow ammonium and sodium salt. This solid, on investigation and analysis, was found to consist of *N*-benzoylsalicylamide and *N*-benzoyl-6-chlorosalicylamide (chiefly the latter) in proportions which varied with different experiments. These two compounds are evidently derived by the action of atmospheric moisture, under the catalytic influence of hydrogen chloride present in small quantity on 2-phenyl-1:3-benzoxazine-4-one and its chloro-derivative formed as by-products in the chlorination.

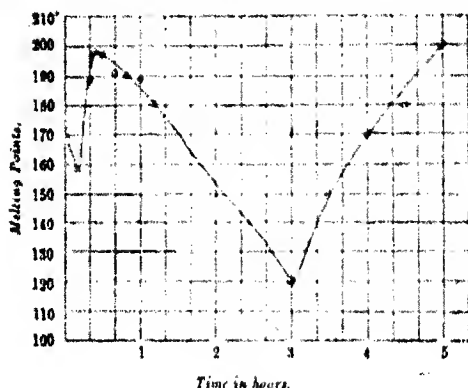
(b) *In Presence of Solvents*.—Chloroform and benzotrichloride were found to be the most suitable solvents for studying the chlorination at different temperatures ( $61^{\circ}$  and  $110^{\circ}$ ).

(1) *Using Chloroform*.—Dry chlorine was passed through a boiling solution of 5 grams of 2-phenyldihydro-1:3-benzoxazine-4-one in 50 grams of chloroform in the dark at a uniform rate of about 4 c.c. per second. At regular intervals a small quantity of the solution was withdrawn, allowed to evaporate on a watch-glass, and the melting point of the resulting solid after washing with cold benzene determined. By plotting the melting points against time, a curve (Fig. 1) was obtained.

The first rise corresponds to the production, with a high velocity, of 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one (m. p.  $214^{\circ}$ ), which reached a maximum in twenty-two minutes. The subsequent

depression, following its conversion with a low velocity into 6-chloro-3-phenyl-1:3-benzoxazine-4-one (m. p. 315°), corresponds with mixtures of the two substances, and the second maximum with the maximum production of the latter compound, melting at 315°. Both reactions take place side by side, and in any case are accompanied by secondary changes which have not been studied, but appear to lead to breaking up of the 1:3-oxazone ring. Hence the two products obtained at the respective melting point maxima are not quite pure, although they are sufficiently so to be purified by recrystallization. On the other hand, it was found to be almost impossible to separate them when mixed in proportions correspond-

FIG. 1.  
*Chlorination in chloroform solution at 61°.*



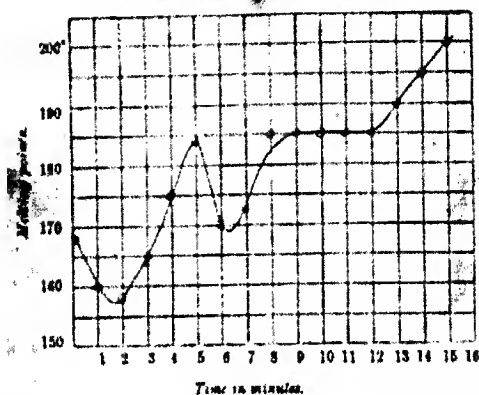
ing with points on the curve other than the maxima, and the conditions of preparation described on p. 1374 were based on the curve.

(2) *Using Benzotrichloride.*—Dry chlorine was passed into a solution of 5 grams of 2-phenyldihydro-1:3-benzoxazine-4-one in 7.5 grams of benzotrichloride at 110° in the dark at a uniform rate of 8 to 9 c.c. per second. The melting points of the solid, obtained from samples withdrawn at one minute intervals, are shown on the curve (Fig. 2), the mean temperature being given in the intervening readings between eight and twelve minutes, where the product melted over a range about 10°. As in the chloroform experiments, the curve shows two maxima, but the velocities of the two reactions are, of course, much higher.

An examination of the product obtained at the first maximum showed that it consisted essentially of the chloro-derivative melting at  $214^{\circ}$ , whilst that obtained at the second maximum consisted essentially of the derivative melting at  $215^{\circ}$ , as in the case of the chloroform experiments, but owing to the increased velocity of the reactions at  $110^{\circ}$  it was found inconvenient to adopt the benzotrichloride process in the preparation of 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one (m. p.  $214^{\circ}$ ), since it is difficult to stop the chlorination at exactly the right point. Chloroform was accordingly used in the preparation of this compound, and benzotrichloride was

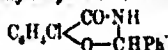
FIG. 2.

Chlorination in benzotrichloride solution at  $110^{\circ}$ .



more conveniently used in the preparation of 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one.

6-Chloro-2-phenyldihydro-1:3-benzoxazine-4-one,



(I) *Preparation by Chlorination Method.*—Dry chlorine was passed into a boiling solution of 20 grams of 2-phenyldihydro-1:3-benzoxazine-4-one in 200 c.c. of chloroform in a reflux apparatus. The action was conducted in a dark chamber, and the gas passed in for twenty minutes at the rate of about 6 c.c. per second, during which hydrogen chloride was liberated in large quantity. The impure chloro-derivative, which crystallised out as a white mass after cooling, weighed 12.5 grams, and melted between  $195^{\circ}$  and

200°. After recrystallization four times from alcohol, it was obtained pure, the melting point remaining constant at 214°.

0.3816, by Kjeldahl's method, required 14.4 c.c. *N*/10-HCl.  
N=5.25.

0.3048 gave 0.1700 AgCl. Cl=13.77.

$C_{12}H_8O_2NCl$  requires N=5.39; Cl=13.69 per cent.

The compound is sparingly soluble in cold alcohol, benzene, or acetone, but readily so in hot alcohol, from which it crystallizes in bundles of fine needles.

**Hydrolysis.**—6-Chloro-2-phenyldihydro-1:3-benzoxazine-4-one is insoluble in cold dilute alkali, but is readily hydrolyzed by the wet reagent, benzaldehyde being produced. One gram was boiled with 10 c.c. of 10 per cent. sodium hydroxide for five minutes, when the solid had completely disappeared. After cooling, alcohol was added, and then excess of dilute hydrochloric acid. After some time, a mass of fine needles separated, melting at 223–224°, which were shown to consist of 5-chlorosalicylamide, the substance being identical in all respects with that obtained (1) by the chlorination of salicylamide (see below), and (2) by pyridine alkali hydrolysis of 5-chloro-2-phenyl-1:3-benzoxazine-4-one (p. 1377).

(2) **Synthetic Preparation of 6-Chloro-2-phenyldihydro-1:3-benzoxazine-4-one.**—The 5-chlorosalicylamide required for the synthesis has been described by Smith (*Ber.*, 1878, 11, 1227), who obtained it from methyl 5-chlorosalicylate. It was prepared by the authors from salicylamide (50 grams in 1500 c.c. of boiling chloroform) by treating it with a rapid stream of dry chlorine in the dark for nearly an hour.

Twenty grams of 5-chlorosalicylamide were mixed with 50 grams of benzaldehyde, and the mixture, after addition of about 1 c.c. of alcoholic hydrogen chloride, was heated to 60–70° for thirty minutes. A clear solution resulted at first, which gradually deposited long, silky needles. On cooling, a mass of crystals was obtained, which were washed carefully with cold alcohol in order to remove the excess of benzaldehyde. The crystals consisted of pure 5-chloro-2-phenyldihydro-1:3-benzoxazine-4-one, and melted at 214°, the yield being 22 grams. After recrystallization from alcohol, the melting point was raised to 215°, and the identity of the compound with that obtained by chlorination (m. p. 214°) was shown by careful comparison, and by the fact that a mixture of the two products melted sharply at 214°.

0.3854, by Kjeldahl's method, required 14.2 c.c. *N*/10-HCl.  
N=5.21.

0.2084 gave 0.1153 AgCl. Cl=13.67.

$C_{12}H_8O_2NCl$  requires N=5.39; Cl=13.69 per cent.

*syn-Benzopidene-5-chlorosacetylamide,*

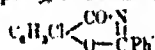
Five grams of 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one in 25 grams of pyridine were shaken with 40 c.c. of 10 per cent. sodium hydroxide for half an hour, by which time the bright yellow colour which at first developed had disappeared. The solution was diluted with water to 2 litres, and treated at  $0^\circ$  with excess of dilute hydrochloric acid. The resulting thick white precipitate, consisting of the *syn*-chloro-derivative, together with a little unchanged compound, was collected, dried in a vacuum and digested with 10 per cent. sodium hydroxide. In this way the very sparingly soluble sodium salt of the *syn*-chloro-derivative was produced, and the white solid, after washing with water to remove traces of 5-chlorosacetylamide (due to slight hydrolysis), was digested with a mixture of equal parts of alcohol and water, in which the sodium salt is readily soluble. The filtrate from the insoluble unchanged cyclic compound, on acidification, gave a white amorphous precipitate of the *syn*-chloro-derivative, which was dried on porous porcelain in a vacuum. It could not be crystallised from solvents without rearrangement to the cyclic isomeride, but analysis showed that it was practically pure:

0.4284, by Kjeldahl's method, required 16.5 c.c.  $N/10\text{-HCl}$ .  $N = 5.40$ .

0.1766 gave 0.0248  $\text{AgCl}$ .  $\text{Cl} = 13.30$ .

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{NCl}$  requires  $N = 5.39$ ;  $\text{Cl} = 13.69$  per cent.

The compound is very sparingly soluble in all solvents except hot alcohol (with rearrangement). It melts at about  $150^\circ$ , also with rapid and complete rearrangement, to 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one, which solidifies in the tube and then melts at  $213^\circ$ . The compound gives a purple coloration in acetone solution with alcoholic ferric chloride.

*6-Chloro-2-phenyl-1:3-benzoxazine-4-one,*

(1) *Preparation by Chlorination Method.*—A rapid stream of dry chlorine (8 to 9 c.c. per second) was passed into a solution of 10 grams of 2-phenyldihydro-1:3-benzoxazine-4-one in 15 grams of benzotrichloride at  $110^\circ$  in the dark for thirty minutes. On cooling, a mass of fine white needles separated after some time, which were collected and washed with small quantities of cold benzene. After recrystallisation, first from benzene and finally from acetone, the

### 1:3-BENZOXAZINE-4-ONE AND RELATED DERIVATIVES 1277

are compound was obtained in long silky needles, melting at  $215^{\circ}$ . When not quite pure, the compound crystallizes in much shorter needles. The yield was 7 grams:

0.4337, by Kjeldahl's method, required 16.5 c.c.  $N/10\text{-HCl}$ .  
 $N=5.24$ .

0.2266 gave 0.1233  $\text{AgCl}$ .  $\text{Cl}=14.06$ .

$\text{C}_{11}\text{H}_8\text{O}_2\text{NCl}$  requires  $N=5.43$ ;  $\text{Cl}=13.78$  per cent.

The compound is somewhat sparingly soluble in hot alcohol, readily so in hot benzene or acetone, but sparingly so in the usual organic solvents in the cold. It is not affected by cold dilute sodium hydroxide, but in contact with strong aqueous ammonia it yields fine orange-yellow needles, which are under investigation. The compound is not sensibly affected by cold dilute acids, but in an alcoholic solution with a little hydrochloric acid, it rapidly undergoes disruption with absorption of water, yielding *N*-benzoyl-5-chlorosalicylamide (m. p.  $235^{\circ}$ ), which separates from the hot liquid as a voluminous microcrystalline mass if the solution is not too dilute. The yield was practically quantitative:

0.2994, by Kjeldahl's method, required 11.8 c.c.  $N/10\text{-HCl}$ .  
 $N=5.26$ .

0.2468 gave 0.1234  $\text{AgCl}$ .  $\text{Cl}=12.37$ .

$\text{C}_{11}\text{H}_8\text{O}_2\text{NCl}$  requires  $N=5.08$ ;  $\text{Cl}=12.88$  per cent.

The substance was identical with the synthetically prepared 5-benzoyl-5-chlorosalicylamide (p. 1380).

#### *Hydrolysis of 6-Chloro-2-phenyl-1:3-benzoxazine-4-one.*

One gram was dissolved in 3 grams of pyridine by warming, and the solution cooled quickly in order to obtain the compound in a fine state of division. The mixture was then treated with 0.5 gram of sodium hydroxide in 100 c.c. of water, and the temperature was raised to  $100^{\circ}$ . An intense yellow colour developed (due to the sodium salt of *N*-benzoyl-5-chlorosalicylamide), which after a few minutes disappeared. The colourless solution was then rapidly cooled, diluted to 300 c.c., and acidified. The precipitated 5-chlorosalicylamide weighed 0.64 gram (theory requires 0.605), and the filtrate, after adding salt and extracting with ether, gave 0.46 gram of benzoic acid melting, after recrystallisation, at  $119^{\circ}$  (theory requires 0.47). The 5-chlorosalicylamide, after recrystallisation from alcohol, was obtained in fine needles, melting at  $224\text{--}225^{\circ}$ :

0.4414, by Kjeldahl's method, required 25.4 c.c.  $N/10\text{-HCl}$ .  
 $N=8.06$ .

0.2800 gave 0.2374  $\text{AgCl}$ .  $\text{Cl}=20.94$ .

$\text{C}_7\text{H}_5\text{O}_2\text{NCl}$  requires  $N=8.16$ ;  $\text{Cl}=20.70$  per cent.



The melting point was not depressed when mixed with the product obtained by chlorinating salicylamide (p. 1375). Further, the position (5) of the chlorine atom was confirmed by prolonged hydrolysis at 100° with sodium hydroxide, the 5-chlorosalicylic acid described by Hübner and Brenken (*Ber.*, 1873, 6, 1237) being obtained.

*Reduction of 6-Chloro-2-phenyl-1:3-benzoxazine-4-one.*

Owing to the sparing solubility of the substance in alcohol or ether, the method of reduction, using aluminium amalgam employed by Titherley (*loc. cit.*) for the parent compound, failed in spite of numerous trials. The following method gave excellent results. One gram of the substance, dissolved in 100 c.c. of pure acetic acid, was treated in the cold with 1.5 grams of zinc dust, and shaken for an hour. After filtering, the clear solution was diluted to 500 c.c. with water, when 6-chloro-2-phenyldihydro-1:3-benzoxazine-4-one separated as a white microcrystalline precipitate. It was quite pure, and melted at 213–214°, and a mixture with the synthetic substance (p. 1375) melted at 213–214°. It gave benzaldehyde on hydrolysis, and the yield was 0.7 gram:

O-1176, by Kjeldahl's method, required 4.6 c.c.  $N/10\text{-HCl}$ .  
N=5.47.

O-1382 gave 0.0806 AgCl. Cl=14.4.

$\text{C}_{12}\text{H}_9\text{O}_2\text{NCl}$  requires N=5.39; Cl=13.69 per cent.

(2) *Synthetic Preparation of 6-Chloro-2-phenyl-1:3-benzoxazine-4-one.*—The synthesis was effected from phenylbenzamidino and phenyl 5-chlorosalicylate; the latter compound described by Curcio (*Gazzetta*, 1898, 28, i, 151) being prepared by a modified method, using chloroform instead of alcohol as a solvent.

Seven grams of phenyl 5-chlorosalicylate and 5 grams of phenylbenzamidino were heated together at 110° for four hours. A clear, yellow oil resulted, which eventually solidified to a large extent, phenol and aniline being liberated as the reaction proceeded. After cooling, the product was extracted with small quantities of benzene to remove phenol and aniline, together with a bright yellow substance, which appeared to be 5-chlorosalicylphenylbenzamidino,  $\text{OH}\cdot\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}$ , but was not isolated. This substance is evidently the first condensation product in the reaction between phenyl 5-chlorosalicylate and phenylbenzamidino (compare Titherley, this vol., p. 204), and by reversible decomposition with loss of aniline yields 6-chloro-2-phenyl-1:3-benzoxazine-4-one, which, on account of its high melting point, separates out as the solid above mentioned. The solid, after washing with benzene, became white,

# 1:3-BENZOXAZINE-4-ONE AND RELATED DERIVATIVES 1379

and on recrystallising, first from hot benzene and finally from acetone, the compound was obtained quite pure in colourless silky needles, melting at 215°. It was identical in properties with the compound prepared by chlorination (p. 1376):

0.3841, by Kjeldahl's method, required 15.0 c.c. *N*/10-HCl.  
N=5.46.

0.1633 gave 0.0946 AgCl. Cl=13.86.

$C_{14}H_8O_2NCl$  requires N=5.43; Cl=13.78 per cent.

(3) *Preparation of 6-Chloro-2-phenyl-1:3-benzoxazine-4-one from O-Benzoyl-5-chlorosalicylamide*.—The method employed was similar to that adopted by Titherley (this vol., p. 208), anisole instead of xylene being used as a solvent. One gram of *O*-benzoyl-5-chlorosalicylamide (see below) in 10 c.c. of anisole was treated at 150° in a small distilling flask with a slow stream of dry hydrogen chloride for three minutes, and the anisole carrying the chemically-formed water slowly distilled off. A yellow syrup remained, which solidified on cooling. By extracting with boiling benzene from a small quantity (0.09 gram) of insoluble *N*-benzoyl-5-chlorosalicylamide, a filtrate was obtained which, on cooling, deposited 6-chloro-2-phenyl-1:3-benzoxazine-4-one in a nearly pure condition, melting at 214°, and weighing 0.8 gram. It was obtained quite easily of (m. p. 215°) by a single recrystallisation from acetone, and found to be identical in all respects with the product obtained by the previous methods:

0.3660, by Kjeldahl's method, required 14.3 c.c. *N*/alkaloids  
N=5.45.

0.3148 gave 0.1752 AgCl. Cl=13.76.

$C_{14}H_8O_2NCl$  requires N=5.43; Cl=13.78 per cent.

*O*-Benzoyl-5-chlorosalicylamide,  $C_{14}H_9ClO_3N$

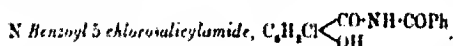
A solution of 20 grams of 5-chlorosalicylamide in 40 grams of pyridine (dried by barium oxide) was treated with 20 grams of benzoyl chloride with continual shaking. The temperature was kept at -15° during the addition, which occupied three hours, and the resulting bright red mixture was kept at -15° for a further hour. It was then shaken with 100 c.c. of dry ether, the ethereal pyridine solution decanted off, and the remaining yellow solid mass treated with dilute sulphuric acid at 0°. The insoluble biscuit-coloured powder which remained, consisting of the crude *O*-benzoyl derivative, after washing with water and ether, weighed 22 grams, and melted at 150°. On recrystallisation from toluene, it separated in fine colourless needles, melting at 153°:

0.6902, by Kjeldahl's method, required 21.8 c.c.  $N/10\text{-HCl}$   $N=5.16$ .

0.2092 gave 0.1636  $\text{AgCl}$ .  $\text{Cl}=12.08$ .

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{NCl}$  requires  $N=5.08$ ;  $\text{Cl}=12.88$  per cent.

*O-Benzoyl-5-chlorosalicylamide* is sparingly soluble in the common organic solvents in the cold. In boiling alcohol it dissolves, but is rapidly rearranged to *N*-benzoyl-5-chlorosalicylamide, which separates from the hot liquid. The same rearrangement occurs on boiling with water, or on melting, and the clear liquid obtained by fusion at  $153^\circ$  sets in about thirty seconds to the solid *N*-benzoyl derivative, which then melts at about  $235^\circ$ .



Two grams (accurately weighed) of *O*-benzoyl-5-chlorosalicylamide were dissolved in the minimum quantity of boiling alcohol, the solution was diluted with 200 c.c. of water at  $80^\circ$ , and the temperature kept at the boiling point for a few minutes. A white, crystalline, microcrystalline precipitate of the pure *N*-benzoyl derivative was obtained, melting sharply at  $238^\circ$ , and weighing 0.117 gram (theory requires 2 grams). The melting point was not altered by recrystallisation from boiling anisole:

0.1382, by Kjeldahl's method, required 13.9 c.c.  $N/10\text{-HCl}$   $N=5.23$ .

(2) 0.4 gave 0.1094  $\text{AgCl}$ .  $\text{Cl}=13.1$ .

4-one.— $\text{C}_{14}\text{H}_{10}\text{O}_2\text{NCl}$  requires  $N=5.08$ ;  $\text{Cl}=12.88$  per cent.

phenyl identity of the compound with the product of hydrolytic (Gassio) of the unsaturated cyclic derivative (p. 1377) was shown using comparison of the physical and chemical properties, and a mixture of the two specimens melted at  $237^\circ$ .

*N-Benzoyl-5-chlorosalicylamide* is very sparingly soluble in all solvents, cold or hot. It may be recrystallised from boiling acetic acid if the operation is rapidly carried out to avoid rearrangement (see below). In all its properties it is very similar to *N*-benzoylsalicylamide, and like it, forms intense yellow sparingly soluble sodium and ammonium salts, from which in aqueous solution acids precipitate the substance in colourless gelatinous form.

With alkali at  $100^\circ$  it is readily hydrolysed, yielding benzoic acid and 5-chlorosalicylamide (m. p.  $224^\circ$ ).

*Rearrangement.* — Like *N*-benzoylsalicylamide, the 5-chloro derivative, on boiling with acetic acid, suffers a reversible rearrangement to the *O*-benzoyl isomeride. One gram was boiled with 25 grams of pure acetic acid for four hours; on cooling, 0.2 gram of

unchanged *N*-benzoyl derivative separated out, and on diluting the filtrate with water 0.7 gram of *O*-benzoyl-3-chlorosalicylamide was obtained (m. p. 148°), which, after recrystallization from toluene, melted at 151°. Its properties were identical with those of the synthetic product (p. 1379).

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### CXXVII.—*The Alkaloids of the Pukatea.*

By BERNARD CRACROFT ANTON.

THE Pukatea (*Laurelia Novae Zealandiae*), one of the most characteristic trees of the northern part of New Zealand, belongs to the *Momimidiaceae*—a small family, most largely represented in the tropics. The genus is confined to South America and New Zealand.

The aromatic nature of the pukatea, and the fact that decoctions of the bark are used by the Maoris for alleviating various disorders, have suggested that the tree contains compounds possibly of medicinal value (see Colenso, *Trans. N.Z. Inst.*, 1868, 1, 51; and Goldie, *ibid.*, 1904, 38, 118).

Attention was first drawn by the author (*N. Z. Dept. of Agriculture, Annual Report*, 1901, p. 284) to the occurrence of alkaloids in the tree, and the peculiar property possessed by the bark of ca. ting, when chewed, a tingling sensation on the tongue was traced to a crystalline alkaloid of definite melting point. More recently the investigation of the bark has been continued. The alkaloid, for which the name *pukateine* is proposed, melts at 200°, and has the composition and molecular weight corresponding with the formula  $C_{17}H_{17}O_3N$ . In the mother liquors obtained in the extraction of pukateine, two other alkaloids are present. Neither of these bases has been obtained in the crystalline state, but the salts of one, for which the name *laureline* ( $C_{19}H_{21}O_3N$ ) is proposed, crystallise well. The third alkaloid, for which the name *laurepukine* is suggested, has been obtained only as an amorphous powder.

#### EXPERIMENTAL.

##### *Isolation of the Alkaloids.*

Seventy-five kilos of bark, freshly collected in the month of July from trees in the Marlborough Sounds, were finely divided and steeped for seven days in alcohol containing 0.5 per cent. of acetic

acid. The alcohol was then pressed off, and this treatment of the bark was repeated three times. From the 98 litres of extract thus obtained, the alcohol was distilled, and the remaining acid aqueous liquors were diluted with boiling water and filtered. The acid filtrate was thoroughly shaken with chloroform, which removed two feebly basic alkaloids. One of these, pukateine, is sparingly soluble in cold alcohol, and was obtained in an almost pure state when the residue from the distillation of the chloroform was stirred with alcohol and kept for some hours.

The second alkaloid, laureline, remained in solution as acetate in the alcohol from which the pukateine had crystallised. The amorphous residue left on evaporating the still acid alcohol was boiled with dilute sulphuric acid, and the hot solution filtered. The sparingly soluble sulphate of laureline crystallised in the filtrate on cooling (pukateine sulphate is easily soluble in dilute sulphuric acid).

A third alkaloid (laurepukine) remained in the acid aqueous liquor from which the acetates of pukateine and laureline had been extracted by chloroform. Sodium hydroxide precipitated the crude alkaloid in the amorphous condition.

A sample of the crushed bark was found to contain 0.7 per cent of approximately pure pukateine—a yield not realised on a large scale, as only 64 grams of the alkaloid were obtained from the 75 kilos. of bark. The content of pukateine appeared to vary at different times of the year. If the bark was allowed to remain in a dry room some months before extraction, the yield was very small.

#### *Pukateine.*

Pure pukateine,  $C_{17}H_{17}O_5N$ , is a white, crystalline alkaloid, melting at  $200^\circ$  (uncorr.), insoluble in water, sparingly soluble in light petroleum, more readily so in ether, chloroform, or absolute alcohol, and very soluble in pyridine. The freshly precipitated amorphous base is very soluble in ether or chloroform. Pukateine is precipitated from its solution by a slight excess of acetic acid, and by iodine in potassium iodide, picric acid, auric chloride, platinic chloride, bromine water, ammonia, Mayer's reagent, disodium hydrogen phosphate, and phosphomolybdic acid. It is soluble in alkali hydroxide solutions, and is reprecipitated on passing a current of carbon dioxide through the solution. In both hydrochloric acid and alkali solutions, hydrolysis of pukateine salts has been observed, the crystalline base being precipitated on dilution and heating. Five preparations were analysed:

1. Recrystallised from alcohol, dried at  $100^\circ$ ; m. p.  $200^\circ$ :

0.0741 gave C 19.64  $CO_2$  and 0.0411  $H_2O$ . C = 72.27; H = 6.17.

2. Recrystallised from alcohol; m. p.  $200^{\circ}$ :  
 0.1259 gave 0.3319  $\text{CO}_2$  and 0.0676  $\text{H}_2\text{O}$ .  $\text{C}=71.89$ ;  $\text{H}=5.97$ .
3. Precipitated in a crystalline state by addition of sodium carbonate to the solution in dilute acetic acid:  
 0.0776 gave 0.20545  $\text{CO}_2$  and 0.0428  $\text{H}_2\text{O}$ .  $\text{C}=72.19$ ;  $\text{H}=6.14$ .
4. Recrystallised from absolute alcohol:  
 0.2588 gave 10.8 c.c.  $\text{N}_2$  at  $23^{\circ}$  and 764 mm.  $\text{N}=4.80$ .
5. 0.2181 " 9.6 c.c.  $\text{N}_2$  "  $20^{\circ}$  " 769 mm.  $\text{N}=5.09$ .  
 $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$  requires  $\text{C}=72.08$ ;  $\text{H}=6.01$ ;  $\text{N}=4.95$  per cent.

#### Molecular-weight Determinations.

0.1604, in 7.12 of phenol, gave  $\Delta t = -0.6^{\circ}$ . M.W. = 277.

0.656 in 16.5 " "  $\Delta t = -0.925^{\circ}$ . M.W. = 317.

$\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$  requires M.W. = 283.

#### Solubilities.

100 parts of boiling alcohol dissolve	4.17 parts of pukateine.
100 " alcohol at $17.5^{\circ}$	" 1.10 " "
100 " boiling ether	" 0.44 " "
100 " ether at $17^{\circ}$	" 0.82 " "

*Optical Activity.*—An alcoholic solution containing 0.6 gram in 100 c.c. gave a rotation of no less than  $-2.64^{\circ}$  in a 2-dcm. tube, whence  $\alpha_D^{20} = -220^{\circ}$ .

*Colour Reactions.*—If a solution of potassium dichromate in concentrated sulphuric acid, prepared as for the strychnine reaction, is brought into contact in not too great excess with a few crystals of pukateine, a persistent purple coloration is produced. If excess of the reagent is applied, a green colour merely results. The colour which the reagent gives with strychnine cannot be confused with that given with pukateine. The former is a bright violet, quickly changing to purple, and finally to a bright red. At one stage the purple colour of the strychnine reaction closely resembles that of pukateine, but the ephemeral nature of the one precludes confusion with the other. Concentrated nitric acid dissolves pukateine, with the formation of a dark red colour closely resembling that given by morphine.

Concentrated sulphuric acid alone produces a dull purple colour with pukateine if heat is gently applied.

If one drop of a very dilute solution of potassium nitrite is added to a solution of pukateine in slight excess of sulphuric acid, a dark reddish-brown or green solution is developed. The base remains unchanged in dilute sulphuric acid solutions.

If a solution of pukateine in sodium hydroxide is kept in an

open test-tube for a few hours, the solution becomes green, and on acidifying with hydrochloric acid and extracting with ether, a purple, ethereal layer results. (The experiment was repeated with the purest pukateine, recrystallised from sodium hydroxide solution.) The amount of colouring matter formed was too small to examine.

On heating small quantities of pukateine with soda-lime or zinc dust, no odour of quinoline or pyridine could be detected.

No methoxy groups could be detected when the substance was examined by Ziesel's method.

Nitric acid in cold glacial acetic acid solution gives rise to a highly acidic nitro-derivative, which dissolves in alkalis, yielding an orange-red solution.

Concentrated sulphuric acid dissolves pukateine slowly when they are triturated together in a mortar, and on diluting the syrupy solution with water an insoluble, amorphous, white compound containing nitrogen is formed.

Hydrochloric acid, heated with one-fifth of its weight of pukateine in a sealed tube at  $110^{\circ}$ , completely converts the pukateine into a glassy mass, insoluble in ordinary solvents.

With water in a sealed tube at  $140^{\circ}$ , no similar effect is produced.

#### *Salts of Pukateine.*

(a) *Salts with Acids.*—The hydrochloride,  $C_{17}H_{17}O_3N.HCl$ , is easily prepared by dissolving the base in hot concentrated hydrochloric acid, and rapidly filtering. On cooling the filtrate, a crystalline hydrochloride separates out. This is collected and dried on a porous plate. The anhydrous salt is obtained by drying at a temperature of  $50^{\circ}$  to  $60^{\circ}$  under diminished pressure:

0.5751 neutralised 18.02 c.c.  $N/10-NaOH$ .  $HCl=11.37$ .

0.1842 " 5.80 c.c.  $N/10-NaOH$ .  $HCl=11.50$ .

0.1651 gave 0.075  $AgCl$ .  $Cl=11.22$ .

$C_{17}H_{17}O_3N.HCl$  requires  $HCl=11.42$ ;  $Cl=11.11$  per cent.

The platinumchloride was prepared by the addition of platinum chloride to the solution of pukateine hydrochloride in water. It was washed with hot water, and dried in a desiccator under diminished pressure:

0.1833 salt gave 0.0298 Pt.  $Pt=20.1$ .

$(C_{17}H_{17}O_3N)_2.H_2PtCl_6$  requires  $Pt=20.0$  per cent.

(b) *Salts with Metals: Potassium and Sodium Salts.*—Pukateine dissolves in solutions of potassium or sodium hydroxides, but if the solution is diluted and boiled, the alkaloid is reprecipitated in characteristic prisms, melting at  $200^{\circ}$ . The addition of solid alkali

hydroxide to the hot concentrated solution eventually causes metallic salts to be precipitated, and the solution, on cooling, sets to a magma of hair-like crystals. After collection on an asbestos filter and drying on a porous tile over sulphuric acid, the crystals gave analytical results agreeing with the formula  $C_{17}H_{18}MO_3N$  ( $M = Na$  or  $K$ ). The salts blacken without melting at a temperature below  $350^\circ$ .

For analysis, the salts were dissolved in dilute alcohol, and titrated with phenolphthalein.

#### *Potassium Salt.*

0.1994 neutralised 6.1 c.c.  $N/10\text{-HCl}$ .  $K = 11.9$ .

$C_{17}H_{18}O_3NK$  requires  $K = 12.15$  per cent.

#### *Sodium Salt.*

0.0919 neutralised 2.95 c.c.  $N/10\text{-HCl}$ .  $Na = 7.4$ .

0.1015 gave 0.0235  $Na_2SO_4$ .  $Na = 7.48$ .

$C_{17}H_{18}O_3NNa$  requires  $Na = 7.54$  per cent.

Professor John Malcolm, of Dunedin, is investigating the pharmacology of the alkaloids of the pukatea, and furnishes the following preliminary note.

"Pukateine itself is apparently inactive, due probably to its insolubility. The hydrochloride is very soluble, and shows some of the typical actions of the alkaloids in general.

"Like strychnine, although in relatively much larger doses (0.25 gram per kilo.), it has a convulsant action on the nerve cells of the spinal cord. In the rabbit the convulsions resemble closely those of strychnine poisoning, but in the frog the effect of the drug on the peripheral neuromuscular apparatus modifies the result, for, although the spasms are easily set up and begin by an intense general contraction of all the muscles of the body, relaxation follows almost immediately. An isolated nerve muscle preparation from such a frog cannot be tetanised by a succession of stimuli—the contraction begins well, but ceases very soon, although the stimulation continues.

"This is probably allied to the general action of alkaloids in paralysing the motor nerve endings in muscle, or it may be regarded as a fatigue phenomenon.

"Apart from such alkaloidal effects, pukateine salts have not been found to possess any marked pharmacological actions. On intravenous injection, the blood pressure falls slightly, the heart beats slowly and forcibly, and death results from respiratory failure, sometimes with great suddenness.



"When the alkaloid is rubbed on the tongue, some localized numbness is felt, and in frogs under the influence of the drug there may be no reflex response from some areas of the skin, whilst other areas give reflexes, but this effect appears late, and is probably due to an action on the nerve cells of the spinal cord."<sup>29</sup>

#### *Laureline.*

The preparation of crude laureline sulphate has already been described. To purify it, the salt was dissolved in hot water, and potassium chromate solution added. On cooling, the chromate was precipitated in yellow, amorphous flocks. The chromate was dissolved in hot sodium hydroxide, cooled, acidified with hydrochloric acid, and the base precipitated by sodium carbonate. This was dissolved in ether, and the ether evaporated. Dilute sulphuric acid converted the syrupy residue from the ether into yellowish-white crystals, which slowly become pink. The sulphate crystallises well from dilute sulphuric acid, the mother liquor turning brown on keeping. The sulphate melts and decomposes at about 105°. Laureline salts give the usual reactions with alkaloid reagents, and have a bitter taste. Four preparations were analysed:

*Laureline sulphate.*—Containing water of crystallisation:

1. The substance was heated to 90° under diminished pressure:  
0.2455 lost 0.0362.  $H_2O = 14.74$ .
2. 0.0839 lost 0.0125.  $H_2O = 14.90$ .
3. 0.3664 .. 0.0554.  $H_2O = 15.12$ .

$(C_{19}H_{21}O_2N)_2 \cdot H_2SO_4 \cdot 7H_2O$  requires  $H_2O = 14.89$  per cent.

1. Dried at 90° under diminished pressure:

0.2151 gave 6.4 c.c.  $N_2$  at 20° and 760 mm.  $N = 3.4$ .

2. Regenerated from the chromate and recrystallised from acidified water; dried at 90° under diminished pressure:

0.12 gave 0.2795  $CO_2$  and 0.067  $H_2O$ .  $C = 63.52$ ;  $H = 6.22$ .

3. Recrystallised from acidified water; dried at 90° under diminished pressure:

0.1702 gave 0.3984  $CO_2$  and 0.1004  $H_2O$ .  $C = 63.84$ ;  $H = 6.56$

0.2127 .. 0.07  $BaSO_4$ .  $S = 4.52$ .

4. 0.202 .. 6.9 c.c.  $N_2$  at 17° and 760 mm.  $N = 3.96$ .

0.1418 .. 0.0513  $BaSO_4$ .  $S = 4.97$ .

$(C_{19}H_{21}O_2N)_2 \cdot H_2SO_4$  requires  $C = 63.33$ ;  $H = 6.11$ ;  $N = 3.90$ ;

$S = 4.44$  per cent.

*Laureline Hydrochloride.*—This salt is easily prepared by dissolving the sulphate in boiling water and adding excess of hydrochloric acid. On cooling, the hydrochloride is precipitated in fine crystals. Two preparations were analysed:

## 1. Air-dried on porous tile:

0.4862 neutralised 5.44 c.c.  $N/10$ -NaOH.  $Cl = 10.39$ .0.3791 gave 0.1157  $AgCl$ .  $Cl = 10.24$ .2. 0.1019 gave 0.0426  $AgCl$ .  $Cl = 10.32$ . $C_{15}H_{21}O_2N.HCl$  requires  $Cl = 10.21$  per cent.*Laureline Nitrate.*0.099 gave 7.2 c.c.  $N_2$  and  $22^\circ$  and 744 mm.  $N = 8.03$ . $C_{15}H_{21}O_2N.HNO_3$  requires  $N = 7.65$  per cent.

Most of the salts of laureline are very soluble in boiling water, but sparingly so in cold water. Several different salts may therefore be made with the same material without much loss. On precipitating the sulphuric acid from the solution of the sulphate with barium chloride in boiling acid solution, laureline hydrochloride separates from the filtrate on cooling. Similarly, on precipitating the chloride in boiling nitric acid solution with silver nitrate, the white, crystalline nitrate is precipitated in the filtrate as it cools, subsequently becoming of a brick red colour.

*Laurepukine.*

The crude, amorphous, dark brown alkaloid, the preparation of which has already been described, was dissolved in dilute acetic acid, and fractionally precipitated by the addition of sodium carbonate. By this means the alkaloid was obtained as an almost colourless powder, which dissolved readily in acids, but from which no crystalline salts were obtained. When prepared in this way, the substance is a yellowish-white powder, which melts indefinitely at about  $100^\circ$  to a resinous mass. Analyses and molecular-weight determinations agree approximately with the formula  $C_{16}H_{19}O_2N$ :

Found,  $C = 70.3$ ;  $H = 6.6$ ;  $N = 4.9$ .  $M.W. = 315$ . $C_{16}H_{19}O_2N$  requires  $C = 70.33$ ;  $H = 6.9$ ;  $N = 5.14$  per cent. $M.W. = 272$ .

In view of the doubtful purity of the substance, great importance must not be attached to these figures. Laurepukine dissolves in benzene, and the solution, on keeping, slowly develops a purple colour.

In conclusion, I must express my thanks to Professor Easterfield for the interest he has taken in this research (which is being continued), and for having defrayed a portion of the cost of the investigation from a grant made to him by the Royal Society of London for researches on the poisonous plants of New Zealand.

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### CXXVIII.—*The Action of Alkalis on Certain Derivatives of Coumarin.*

By ARTHUR CLAYTON, B.Sc., A.R.C.S.

THE two most important reactions between alkalis and the aromatic lactones of the coumarin series are the formation of the sodium salt of a coumarinic acid simply by dissolving the coumarin in aqueous sodium hydroxide, and the production of the corresponding o-coumaric acid by the prolonged action of alcoholic solutions of the alkali. The former change is of special interest, because the constitution of coumarinic acid must still be regarded as uncertain, and because it has not yet been found possible to isolate the acid from its salts. The only derivative of coumarinic acid which has heretofore been obtained in the free state is 8-nitrocoumarinic acid, obtained by dissolving 8-nitrocoumarin in aqueous sodium hydroxide, and subsequently acidifying the solution at a low temperature (Miller and Kinkelin, *Ber.*, 1889, **22**, 1706). This acid is very unstable, being resolved into 8-nitrocoumarin and water when warmed with alcohol or water.

In the present communication an account is given of a general investigation of the action of alkalis on substituted coumarins, and more particularly in connexion with the various nitrocoumarins. In order to obtain nitrocoumarins with the nitro-groups in different positions, several of the alkylated coumarins previously prepared by the author (*Trans.*, 1908, **93**, 2016) were nitrated, the entrant groups being forced into desired positions by the alkyl groups already present. In addition to the nitrocoumarins, other coumarins with different substituents were examined, and incidentally it became possible to trace the influence of alkyl groups. The orientation of many of the compounds obtained during the present investigation presented considerable difficulty, owing to the paucity of knowledge of the derivatives of the homologues of coumarin.

#### *The Nitro-derivatives of Coumarin.*

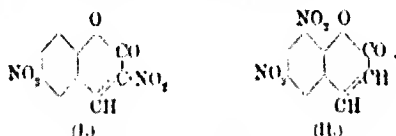
The only nitrocoumarins described in the literature are 6-nitrocoumarin, obtained by the direct nitration of coumarin (Delalande, *Annalen*, 1843, **45**, 337), and 8-nitrocoumarin, the product obtained by heating together 3-nitroacetaldehyde, sodium acetate, and acetic anhydride (Miller and Kinkelin, *loc. cit.*).

Since 8-nitrocoumarin forms an unstable coumarinic acid when its alkaline solution is cautiously acidified, and this formation appears to depend on the presence and position of the nitro-group,

it appeared probable that 6:8-dinitrocoumarin would yield a more stable coumarinic acid when similarly treated. With the object of preparing this acid for future investigation, coumarin was treated with nitric acid under various conditions. Coumarin was found to resist strongly the introduction of more than one nitro-group (p. 1397), but this resistance diminishes very appreciably with the addition of alkyl groups to the molecule. A dinitrocoumarin was finally obtained, melting at 180–181°.

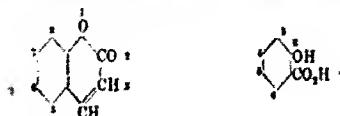
*Orientation of the Dinitrocoumarin (m. p. 180–181°) obtained by Nitrating Coumarin.*

One of the nitro-groups was known to occupy position 6,\* as the dinitrocoumarin could also be prepared by further nitrating 6-nitrocoumarin. The second nitro-group was expected to enter position 8. An attempt was therefore made to prepare the dinitrocoumarin by nitrating 8-nitrocoumarin, but the dinitrocoumarin obtained by this operation melted at 159–160°. The compound melting at 180–181° was therefore oxidised with alkaline potassium permanganate, and yielded 5 nitrosalicylic acid.\* The dinitration of coumarin therefore furnishes a product containing one nitro-group in position 6, and the other in the lactonic ring. The exact position of the lactonic nitro group is shown by the action of sodium hydroxide to be position 3 (see below). The dinitrocoumarin (m. p. 180–181°) produced by the direct nitration of coumarin is therefore 3:6-dinitrocoumarin (formula I):



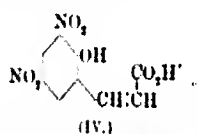
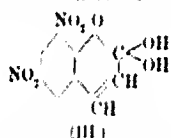
The dinitrocoumarin (m. p. 159–160°) produced by nitrating 8-nitrocoumarin is shown by its action with sodium hydroxide (p. 1390) not to contain a nitro-group in the lactonic ring, and since the nitro-group always enters position 6 if this be open, the compound must be 6:8-dinitrocoumarin (formula II).

\* The method of numbering the positions in the coumarin and salicylic acid molecules is indicated in the following formulae:



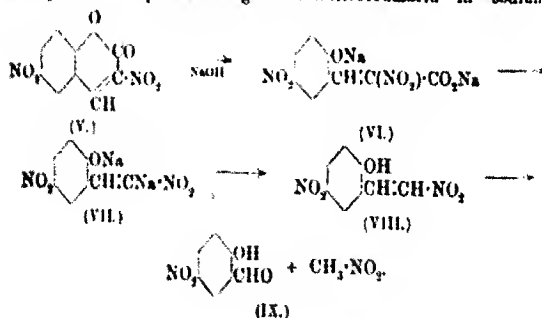
*The Action of Alkalies on the Dinitrocumarins.*

**6: 8-Dinitrocumarin.**—This compound dissolves in weak aqueous sodium hydroxide to a deep orange-red liquid, which, when acidified with cold dilute hydrochloric acid, furnishes a yellow precipitate, melting at about 135°, with a copious evolution of vapour. This substance was shown to be different from 6: 8-dinitrocumarin by the method of mixed melting points. The new compound was also much more soluble in alcohol and water than 6: 8-dinitrocumarin but was rapidly changed into the latter compound when heated with either of these solvents. These facts indicate that the new substance is 6: 8-dinitrocumarinic acid, and this conclusion is confirmed by the very similar properties possessed by 8-nitrocumarinic acid (Miller and Kinkelin, *loc. cit.*). The formula of the new coumarinic acid is therefore III or IV, according as to whether the hypothetical coumarinic acid is regarded as a derivative of carbonic acid or a *cis*-isomeride of *o*-coumaric acid:



**3: 6-Dinitrocumarin.**—When warmed with aqueous sodium hydroxide, or preferably concentrated ammonia solution, 3: 6-dinitrocumarin dissolves to a deep orange-red liquid, which, on subsequent acidification with hydrochloric acid, yields 5-nitrosalicyl aldehyde. This remarkably easy rupture of the lactonic ring was subsequently found to be a property conferred on all coumarins by the presence of a nitro-group in position 3.

In order to trace the course of the above reaction, the sodium salt produced by dissolving 3: 6-dinitrocumarin in sodium



hydroxide was isolated, and found to be the sodium salt of 5-nitrosalicylaldehyde. No other intermediate product was obtained, but in the case of a 4-methyl substituted 3:6-dinitrocoumarin, the styrene derivatives corresponding with formulae VII and VIII were isolated (see p. 1392). The reaction resulting in the formation of 5-nitrosalicylaldehyde is thus shown to follow the course outlined by formulae V—IX (p. 1390).

The whole of the degradation takes place before the addition of the acid, the latter merely liberating the aldehyde from its salt.

It is worthy of note that when benzaldehyde and nitromethane are heated together, *m*-nitrostyrene is produced (Priests, *Annalen*, 1884, 225, 321).

*The Nitro-derivatives of 7-Methylcoumarin and  
4:7-Dimethylcoumarin.*

The nitro-derivatives of 7-methylcoumarin and 4:7-dimethylcoumarin and the dinitro-derivative of 7-methylcoumarin were prepared similarly to the corresponding compounds of coumarin itself. The dinitration of 4:7-dimethylcoumarin proceeded readily at the ordinary temperature, the presence of a methyl group in position 4 appearing very greatly to facilitate the entry of the second nitro-group. The orientation of the nitro-derivatives of this series was accomplished in the manner outlined by formulae X—XVII. 4-Nitro-*p*-xylenol (X) was oxidized by alkaline potassium permanganate to 5-nitro-4-methylsalicylic acid (XI). This acid was then produced by the oxidation of each of the four nitro-derivatives under examination. The nitro-derivatives of 7-methylcoumarin and 4:7-dimethylcoumarin are thus shown to be 6-nitro-7-methylcoumarin (XII) and 6-nitro-4:7-dimethylcoumarin (XIV) respectively. The corresponding dinitro-derivatives are also shown to contain a nitro-group in position 6, and a second in the lactonic ring. The exact position of the second nitro-group is proved by the action of sodium hydroxide (see below).

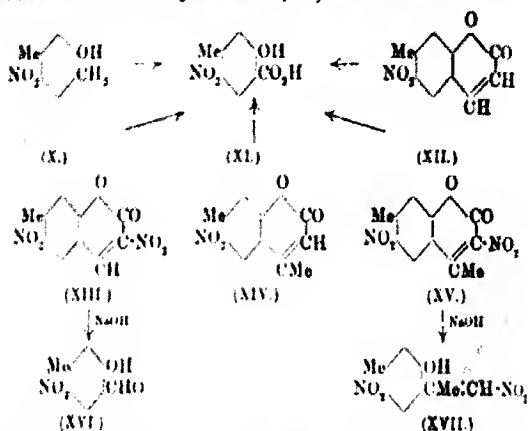
*The Action of Alkalis on the Products of Nitration of 7-Methylcoumarin and 4:7-Dimethylcoumarin.*

6-Nitro-7-methylcoumarin and 6-nitro-4:7-dimethylcoumarin dissolve in aqueous sodium hydroxide, the former more readily than the latter, forming orange solutions, which, however, when carefully acidified, only regenerate the original nitro-compounds.

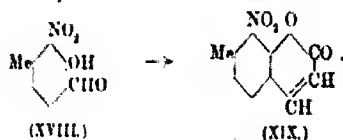
The dinitro-derivative of 7-methylcoumarin forms with aqueous sodium hydroxide an orange-red solution, which, when acidified, yields 5-nitro-4-methylsalicylaldehyde (XVI), of which the oxime

and phenylhydrazine were prepared. The above dinitro-derivative is therefore shown to be 3:6-dinitro-7-methylcoumarin (XIII).

The dinitro-derivative of 4:7-dimethylcoumarin dissolves in aqueous sodium hydroxide to an orange liquid, which, when carefully acidified, yields *o*-5-dinitro-2-hydroxy-*o*-4-dimethylstyrene (XVII). The parent dinitro-derivative is thus shown to be 3:6-dinitro-4:7-dimethylcoumarin (XV):



Before the above orientations had been worked out, the constitution of 6-nitro-7-methylcoumarin had been indicated by nitrating 4-methylsalicylaldehyde and heating the resulting 3-nitro-4-methylsalicylaldehyde (XVIII) with sodium acetate and acetic anhydride, thereby obtaining 6-nitro-7-methylcoumarin (XIX). The latter compound was then shown to be different from the nitration product of 7-methylcoumarin, thus indicating this nitration product to be 6-nitro-7-methylcoumarin:



*The Nitration Products of 6:7-Dimethylcoumarin and 4:6:7-Trimethylcoumarin.*

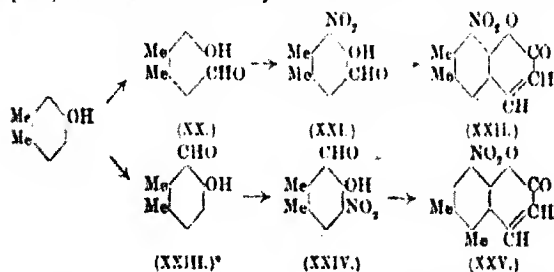
6:7-Dimethylcoumarin yields mono, di, and tri-nitro-derivatives at the ordinary temperature. 4:6:7-Trimethylcoumarin was nitrated with even greater ease, an extraordinary readiness to form

the trinitro-derivative being manifested. So great was this tendency that it was not found possible to prepare the dinitro-derivative. From these and the foregoing results there can be no doubt that the difficulty of obtaining the higher nitration products of coumarin is due to the general acidity conferred on the molecule by the lactonic ring, and that the introduction of methyl groups gradually weakens this acidity and makes the molecule more susceptible to the action of nitric acid. A methyl group in the lactonic ring is seen to be specially efficacious in this respect.

The orientation of the nitration products of this series could not be effected by methods of oxidation. The following process was therefore adopted for the orientation of the nitro-derivative of 6:7-dimethylcoumarin.

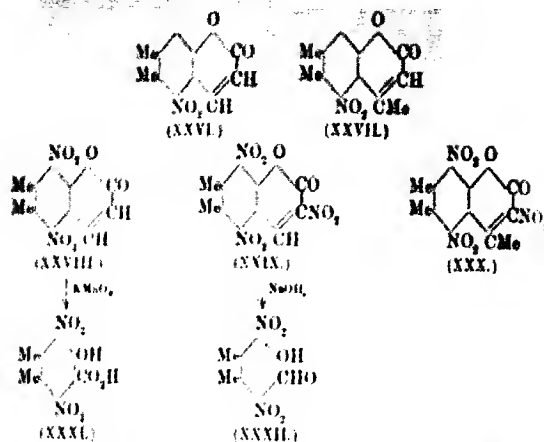
Since this compound does not behave towards sodium hydroxide in the manner characteristic of coumarins with a nitro group in the lactonic ring, the nitro group must occupy position 5 or 8.

*o*-4-Xylenol was submitted to the Tiemann reaction, and yielded a product which, when crystallised from light petroleum, separated into long, spiky needles and pearly flakes. These crystals were separated mechanically, and separately recrystallised from light petroleum. Both compounds melted at 71–72°, and formed compounds with sodium hydrogen sulphite, but were shown to be different by the method of mixed melting points. The oxidation of the flaky compound by fused potassium hydroxide yielded 4:5-dimethylsalicylic acid, thus proving the aldehyde crystallising in flakes to be 4:5-dimethylsalicylaldehyde (XX). The latter compound, on nitration, yields 3-nitro-4:5-dimethylsalicylaldehyde (XXI), which was converted by the Perkin reaction into 8-nitro-



\* In order to complete the study of this branch of the coumarins, the second compound (acicular crystals) obtained from *o*-4-xylenol was first shown to be 5:6-dimethylsalicylaldehyde (XXIII) by preparing its sodium hydrogen sulphite compound, and by oxidising it to 5:6-dimethylsalicylic acid. The aldehyde was then nitrated, yielding 3-nitro-5:6-dimethylsalicylaldehyde (XXIV), which was converted by the Perkin reaction into 8-nitro-4:5-dimethylcoumarin (XXV).





6: 7-dimethylcoumarin (XXII). The latter compound proved to be different from the substance obtained by nitrating 6: 7-dimethylcoumarin, therefore this nitration product must be 5-nitro-6: 7-dimethylcoumarin (XXVI), and from analogy the nitro-derivative of 4: 6: 7-trimethylcoumarin is 5-nitro-4: 6: 7-trimethylcoumarin (XXVII).

The orientation of the dinitro-derivative of 6: 7-dimethylcoumarin was effected by oxidation with alkaline potassium permanganate, this operation yielding 3: 6-dinitro-4: 5-dimethylsalicylic acid (XXXI), thus showing the compound under examination to be 5: 8-dinitro-6: 7-dimethylcoumarin (XXVIII).

The trinitro-derivatives of 6: 7-dimethylcoumarin and 4: 6: 7-trimethylcoumarin must contain a nitro-group in the lactonic ring, and are therefore 3: 5: 8-trinitro-6: 7-dimethylcoumarin (XXIX) and 3: 5: 8-trinitro-4: 6: 7-trimethylcoumarin (XXX). The behaviour of these compounds towards sodium hydroxide (see below) confirms this view.

*The Action of Alkalis on the Products of Nitration of  
6: 7-Dimethylcoumarin and 4: 6: 7-Trimethylcoumarin.*

5-Nitro-6: 7-dimethylcoumarin and 5-nitro-4: 6: 7-trimethylcoumarin dissolve slightly in aqueous sodium hydroxide, the latter less readily than the former, yielding orange-yellow solutions, from which acidification regenerates the nitro-derivatives. 5: 8-Dinitro-6: 7-dimethylcoumarin dissolves readily in aqueous sodium hydroxide to an orange-red solution, which, on acidification at  $-5^{\circ}$ , yields a

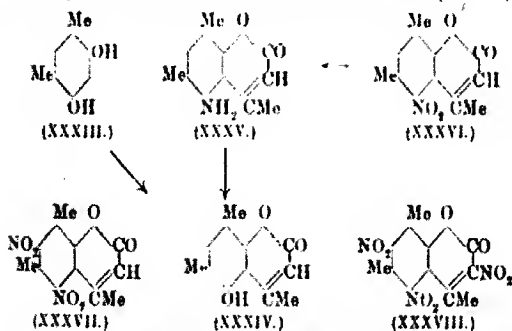
compound melting at about  $165^{\circ}$  with a copious evolution of vapour. On recrystallising this compound from alcohol, or even keeping it in the dry state for a few hours, 5:8-dinitro-6:7-dimethylcoumarin is regenerated. The precipitate obtained as above is probably an extremely unstable coumarinic acid.

3:5:8-Trinitro-6:7-dimethylcoumarin dissolves readily in aqueous sodium hydroxide to an orange-red solution, which, when acidified, yields 3:6-dinitro-4:5-dimethylsalicylaldehyde (XXXII). The course of the reaction is therefore strictly analogous with that outlined by formulae V—IX.

3:5:8-Trinitro-4:6:7-trimethylcoumarin dissolves in aqueous sodium hydroxide to an orange-red solution, but no definite compound was isolated from the sticky material produced on acidification.

*The Nitro-derivatives of 4:6:8-Trimethylcoumarin.*

4:6:8-Trimethylcoumarin yields mono-, di-, and tri-nitro-derivatives at the ordinary temperature. The orientation of these nitro-derivatives could not be carried out by methods of oxidation. The constitution of the nitro-derivative of 4:6:8-trimethylcoumarin was accomplished in the manner indicated by formulae XXXIII—XXXVI. 4:6-Dimethylresorcinol (XXXIII) was condensed with ethyl acetoacetate, yielding 5-hydroxy-4:6:8-trimethylcoumarin (XXXIV). The latter compound was then prepared from the nitro-derivative of 4:6:8-trimethylcoumarin by reducing it to the corresponding amine, and converting this compound through its diazonium chloride into 5-hydroxy-4:6:8-trimethylcoumarin. The nitro-derivative of 4:6:8-trimethylcoumarin is therefore 5-nitro-4:6:8-trimethylcoumarin (XXXVI), and its reduction product, 5-amino-4:6:8-trimethylcoumarin (XXXV):



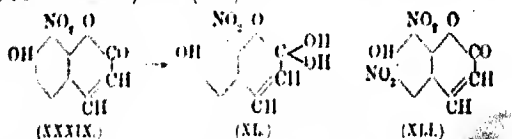
The dinitro-derivative of 4:6:8-trimethylcoumarin is practically

unaffected by aqueous sodium hydroxide; hence it does not contain a nitro-group in the lactonic ring, and must be 5:7-dinitro-4:6:8-trimethylcoumarin (XXXVI). The trinitro-derivative can only be 3:5:7-trinitro-4:6:8-trimethylcoumarin (XXXVIII).

5-Nitro-4:6:8-trimethylcoumarin and 5:7-dinitro-4:6:8-trimethylcoumarin remain practically unattacked when boiled with aqueous sodium hydroxide. 3:5:7-Trinitro-4:6:8-trimethylcoumarin dissolves in this reagent to an orange-red liquid, which, however, yields no crystalline product on acidification.

*The Nitro-derivatives of 7-Hydroxycoumarin (Umbelliferone).*

The only nitro-derivative of umbelliferone mentioned in the literature is trinitroumbelliferone (Popen, *Ber.*, 1881, 14, 2747), which does not appear to have been orientated, but which is described as being decomposed by sodium hydroxide. It is therefore very possibly 3:6:8-trinitroumbelliferone. The author of the present communication prepared nitro- and dinitro-umbelliferone, the action proceeding at the ordinary temperature. From analogy to the corresponding nitro-derivatives of 4-methylumbelliferone, the compounds in question are 8-nitroumbelliferone (XXXIX) and 6:8-dinitroumbelliferone (XLI):



Aqueous sodium hydroxide dissolves 8-nitroumbelliferone (yellow) to a red liquid, furnishing, on acidification, a scarlet precipitate of 8-nitrocoumarinic acid, which, if the carbonic acid formula be adopted, has the constitution indicated by (XL). This coumarinic acid is the most stable of those yet discovered, and may easily be crystallised from dry ether. When heated, however, it slowly reverts to 8-nitroumbelliferone.

6:8-Dinitroumbelliferone dissolves easily in aqueous sodium hydroxide, but is regenerated when the solution is acidified.

*Summary.*

1. A number of nitration products of coumarin and its homologues have been prepared and orientated.
2. Position 3 in the lactonic ring has been shown to be peculiarly susceptible to the action of nitric acid, the nitro-group often entering this position when other positions are open in the benzenoid

3. Coumarins containing a nitro-group in position 8, and unsubstituted in the lactonic ring, show a tendency to form free coumarinic acids. This tendency is decreased by the presence of alkyl groups in the molecule.

4. Several coumarinic acids have been prepared. They are all more or less unstable.

5. Coumarins containing a nitro-group in position 3, and not substituted in position 4, yield aldehydes when treated with sodium hydroxide. This reaction has been investigated in several typical cases, and forms a new method for preparing aromatic hydroxy-aldehydes.

6. Coumarins containing a nitro-group in position 3, and an alkyl group in position 4, react with sodium hydroxide to form the corresponding *m*-nitrostyrene.

#### EXPERIMENTAL

##### 1.—The Nitration of Coumarin and its Homologues.

###### *The Nitroderivatives of Coumarin.*

3: 6-Dinitrocoumarin.—6-Nitrocoumarin (4 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and treated with a nitrating mixture\* at a temperature below 5°. The resulting liquid, after remaining at the ordinary temperature for one hour, was gradually heated to 100°, and maintained at this temperature for twenty minutes. The cooled solution was then poured on ice, and the solid which separated was collected. After two or three crystallisations from glacial acetic acid, yellow needles were obtained, melting at 180–181°:

0.1227 gave 0.2063 CO<sub>2</sub> and 0.0203 H<sub>2</sub>O. C=45.85; H=1.84.

0.1061 „ 10.8 c.c. N<sub>2</sub> at 19° and 756 mm. N=11.81.

C<sub>9</sub>H<sub>6</sub>O<sub>4</sub>N<sub>2</sub> requires C=45.76; H=1.69; N=11.86 per cent.

6: 8-Dinitrocoumarin, prepared by nitrating 8-nitrocoumarin in the foregoing manner, crystallised from glacial acetic acid in yellow needles, melting at 159–160°:

0.0958 gave 0.1613 CO<sub>2</sub> and 0.0173 H<sub>2</sub>O. C=45.93; H=2.01.

0.1068 „ 11.4 c.c. N<sub>2</sub> at 21° and 750 mm. N=11.99.

C<sub>9</sub>H<sub>6</sub>O<sub>4</sub>N<sub>2</sub> requires C=45.76; H=1.69; N=11.86 per cent.

##### *The Nitro-derivatives of 7-Methylcoumarin and 4: 7-Dimethylcoumarin.*

6-Nitro-7-methylcoumarin.—7-Methylcoumarin (4 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and treated at 0°

\* The "nitrating mixture" used throughout these experiments consisted of 1 volume of nitric acid (D 1.4) and 3 volumes of concentrated sulphuric acid.

with the nitrating mixture (5 c.c.). The liquid was kept at the ordinary temperature for one hour, and then poured on ice, when a white solid separated, which crystallised from glacial acetic acid in white needles, melting at  $222-224^{\circ}$ :

0.1939 gave 0.4143  $\text{CO}_2$  and 0.0625  $\text{H}_2\text{O}$ .  $\text{C}=58.27$ ;  $\text{H}=3.58$ .

0.2587 .. 15.2 c.c.  $\text{N}_2$  at  $23^{\circ}$  and 748 mm.  $\text{N}=6.52$ .

$\text{C}_{10}\text{H}_7\text{O}_4\text{N}$  requires  $\text{C}=58.53$ ;  $\text{H}=3.41$ ;  $\text{N}=6.83$  per cent.

3: 6-Dinitro-7-methylcoumarin. — 6-Nitro-7-methylcoumarin (3 grams), dissolved in concentrated sulphuric acid (10 c.c.), was treated at  $0^{\circ}$  with the nitrating mixture (5 c.c.). The solution was kept at the ordinary temperature for one hour, and then gradually heated to  $100^{\circ}$ , at which temperature it was maintained for twenty minutes. The cooled liquid was poured on ice, and yielded a product which crystallised from glacial acetic acid in yellow needles, melting at  $164-165^{\circ}$ :

0.2316 gave 0.4097  $\text{CO}_2$  and 0.0545  $\text{H}_2\text{O}$ .  $\text{C}=48.24$ ;  $\text{H}=2.61$ .

0.2093 .. 21.4 c.c.  $\text{N}_2$  at  $24^{\circ}$  and 753 mm.  $\text{N}=11.35$ .

$\text{C}_{10}\text{H}_6\text{O}_4\text{N}_2$  requires  $\text{C}=48.00$ ;  $\text{H}=2.40$ ;  $\text{N}=11.20$  per cent.

6-Nitro-4: 7-dimethylcoumarin. — 4: 7-Dimethylcoumarin (4 grams), dissolved in concentrated sulphuric acid (20 c.c.), was treated at  $0^{\circ}$  with the nitrating mixture (7.5 c.c.). After remaining at the ordinary temperature for one hour, the liquid was poured on ice, when a white solid separated, which crystallised from glacial acetic acid in colourless needles, melting at  $252-253^{\circ}$ :

0.1804 gave 0.4000  $\text{CO}_2$  and 0.0718  $\text{H}_2\text{O}$ .  $\text{C}=60.48$ ;  $\text{H}=4.42$ .

0.1944 .. 10.4 c.c.  $\text{N}_2$  at  $15^{\circ}$  and 773 mm.  $\text{N}=6.37$ .

$\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}$  requires  $\text{C}=60.27$ ;  $\text{H}=4.11$ ;  $\text{N}=6.39$  per cent.

3: 6-Dinitro-4: 7-dimethylcoumarin. — 4: 7-Dimethylcoumarin (4 grams) was dissolved in concentrated sulphuric acid (20 c.c.), and slowly treated at  $0^{\circ}$  with the nitrating mixture (12 c.c.). The liquid was kept overnight, and then poured on ice; the white precipitate crystallised from glacial acetic acid in colourless needles, melting and decomposing at about  $235^{\circ}$ :

0.1353 gave 0.2494  $\text{CO}_2$  and 0.0400  $\text{H}_2\text{O}$ .  $\text{C}=50.28$ ;  $\text{H}=3.28$ .

0.2056 .. 18.6 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 764 mm.  $\text{N}=10.40$ .

$\text{C}_{11}\text{H}_8\text{O}_4\text{N}_2$  requires  $\text{C}=50.00$ ;  $\text{H}=3.03$ ;  $\text{N}=10.61$  per cent.

*The Nitro-derivatives of 6: 7-Dimethylcoumarin and 4: 6: 7-Tri-methylcoumarin.*

8-Nitro-6: 7-dimethylcoumarin. — 6: 7-Dimethylcoumarin (34 grams), dissolved in concentrated sulphuric acid (30 c.c.), was treated at  $0^{\circ}$  with the nitrating mixture (7.5 c.c.), and the resulting liquid kept at the ordinary temperature for one hour. The solution

was then poured on ice, when a solid was obtained which, after crystallisation from glacial acetic acid, formed white needles, melting at  $210-211^{\circ}$ :

0.1130 gave 0.2491  $\text{CO}_2$  and 0.0457  $\text{H}_2\text{O}$ .  $\text{C}=60.12$ ;  $\text{H}=4.49$ .

0.3000 " 16.9 c.c.  $\text{N}_2$  at  $24^{\circ}$  and 747 mm.  $\text{N}=6.21$ .

$\text{C}_{11}\text{H}_9\text{O}_4\text{N}$  requires  $\text{C}=60.27$ ;  $\text{H}=4.11$ ;  $\text{N}=6.39$  per cent.

5: 8-Dinitro-6: 7-dimethylcoumarin.—6: 7-Dimethylcoumarin (2.4 grams) was dissolved in concentrated sulphuric acid (25 c.c.), treated at  $0^{\circ}$  with the nitrating mixture (8.8 c.c.), and the liquid kept overnight at the ordinary temperature. It was then poured on ice, when a solid was obtained which crystallised from glacial acetic acid in pale yellow needles, melting at  $175-176^{\circ}$ . The yellow colour was completely removed by boiling with 50 per cent. acetic acid and a little animal charcoal. The substance possesses a peculiar and characteristic odour:

0.1347 gave 0.2457  $\text{CO}_2$  and 0.0415  $\text{H}_2\text{O}$ .  $\text{C}=49.74$ ;  $\text{H}=3.43$ .

0.0945 " 9.1 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 764 mm.  $\text{N}=11.07$ .

$\text{C}_{11}\text{H}_9\text{O}_6\text{N}_2$  requires  $\text{C}=50.00$ ;  $\text{H}=3.03$ ;  $\text{N}=10.61$  per cent.

3: 5: 8-Trinitro-6: 7-dimethylcoumarin.—6: 7-Dimethylcoumarin (5 grams) was dissolved in concentrated sulphuric acid (40 c.c.), and treated with the nitrating mixture (26 c.c.) exactly as in the preceding experiment. The product obtained crystallised from glacial acetic acid in yellow prisms, melting and decomposing at  $213-216^{\circ}$ :

0.1658 gave 0.2607  $\text{CO}_2$  and 0.0351  $\text{H}_2\text{O}$ .  $\text{C}=42.88$ ;  $\text{H}=2.35$ .

0.1844 " 19.1 c.c.  $\text{N}_2$  at  $22^{\circ}$  and 749 mm.  $\text{N}=13.82$ .

$\text{C}_{11}\text{H}_7\text{O}_9\text{N}_3$  requires  $\text{C}=42.72$ ;  $\text{H}=2.27$ ;  $\text{N}=13.59$  per cent.

8-Nitro-4: 6: 7-trimethylcoumarin.—A solution of 4: 6: 7-trimethylcoumarin (11 grams) in concentrated sulphuric acid (110 c.c.) was slowly treated at  $0^{\circ}$  with the nitration mixture (20 c.c.), and then kept at the ordinary temperature for thirty minutes, after which the liquid was poured on ice. A white product was precipitated, which crystallised from glacial acetic acid in colourless needles, melting at  $186-187^{\circ}$ :

0.2204 gave 0.4958  $\text{CO}_2$  and 0.0946  $\text{H}_2\text{O}$ .  $\text{C}=61.36$ ;  $\text{H}=4.77$ .

0.2784 " 14.8 c.c.  $\text{N}_2$  at  $22^{\circ}$  and 761 mm.  $\text{N}=6.04$ .

$\text{C}_{17}\text{H}_{11}\text{O}_4\text{N}$  requires  $\text{C}=61.80$ ;  $\text{H}=4.72$ ;  $\text{N}=6.01$  per cent.

3: 5: 8-Trinitro-4: 6: 7-trimethylcoumarin.—A solution of 4: 6: 7-trimethylcoumarin (2 grams) in concentrated sulphuric acid (10 c.c.) was treated with the nitrating mixture (10 c.c.) as in the preceding experiment. A crystalline mass formed in the acid solution. After precipitation by pouring into ice-water and crystallisation from glacial acetic acid, the product formed beauti-

white, faintly yellow plates, melting and decomposing at about 170°. Darkening took place immediately above this temperature.

0.1365 gave 0.2116  $\text{CO}_2$  and 0.0364  $\text{H}_2\text{O}$ .  $\text{C}=44.58$ ;  $\text{H}=2.11$ .

0.1723 " 20.0 c.c.  $\text{N}_2$  at 22° and 766 mm.  $\text{N}=13.00$ .

$\text{C}_{12}\text{H}_9\text{O}_4\text{N}_2$  requires  $\text{C}=44.58$ ;  $\text{H}=2.79$ ;  $\text{N}=13.00$  per cent.

#### *The Nitro-derivatives of 4:6:8-Trimethylcoumarin.*

**5-Nitro-4:6:8-trimethylcoumarin.** — 4:6:8-Trimethylcoumarin (7 grams) was dissolved in concentrated sulphuric acid (35 c.c.), and treated with the nitrating mixture (15.2 c.c.) at 0°, after which the liquid was kept at the ordinary temperature for thirty minutes and then poured on ice. The product separated from its solution in glacial acetic acid in white needles, melting at 140–141°, and having a peculiar odour:

0.1808 gave 0.4127  $\text{CO}_2$  and 0.0802  $\text{H}_2\text{O}$ .  $\text{C}=62.24$ ;  $\text{H}=4.95$ .

0.1727 " 9.5 c.c.  $\text{N}_2$  at 22° and 766 mm.  $\text{N}=6.28$ .

$\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}$  requires  $\text{C}=61.80$ ;  $\text{H}=4.72$ ;  $\text{N}=6.01$  per cent.

**6:7-Dinitro-4:6:8-trimethylcoumarin.** — 4:6:8-Trimethylcoumarin (5 grams) was dissolved in concentrated sulphuric acid, and treated at 0° with the nitrating mixture (16 c.c.). The liquid was kept for three hours, and then poured into ice-water, when a product was obtained which, after crystallisation from 50 per cent. acetic acid, formed almost white needles, melting at 194°:

0.1659 gave 0.3153  $\text{CO}_2$  and 0.0607  $\text{H}_2\text{O}$ .  $\text{C}=51.92$ ;  $\text{H}=4.06$ .

0.1408 " 12.6 c.c.  $\text{N}_2$  at 24° and 768 mm.  $\text{N}=10.15$ .

$\text{C}_{12}\text{H}_{10}\text{O}_5\text{N}_2$  requires  $\text{C}=51.79$ ;  $\text{H}=3.60$ ;  $\text{N}=10.07$  per cent.

**3:5:7-Trinitro-4:6:8-trimethylcoumarin.** — A solution of 4:6:8-trimethylcoumarin (4 grams) in concentrated sulphuric acid (20 c.c.) was treated at 0° with the nitrating mixture (20 c.c.), as in the preceding experiment. The product crystallised from glacial acetic acid in pale yellow needles, melting and decomposing at about 190°:

0.2272 gave 0.3749  $\text{CO}_2$  and 0.0500  $\text{H}_2\text{O}$ .  $\text{C}=45.00$ ;  $\text{H}=2.44$ .

0.1632 " 18.9 c.c.  $\text{N}_2$  at 22° and 766 mm.  $\text{N}=13.23$ .

$\text{C}_{12}\text{H}_8\text{O}_6\text{N}_3$  requires  $\text{C}=44.58$ ;  $\text{H}=2.79$ ;  $\text{N}=13.00$  per cent.

**7-Nitro-6:6:8-trimethylcoumarin.** — 5:6:8-Trimethylcoumarin (7.5 grams) was dissolved in concentrated sulphuric acid (8 c.c.), and treated at 5° with the nitrating mixture (3.6 c.c.). After one hour the liquid was poured on ice, when a solid was produced which crystallised from glacial acetic acid in white needles, melting at 151°:

0.1332 gave 0.2790  $\text{CO}_2$  and 0.0479  $\text{H}_2\text{O}$ .  $\text{C}=61.77$ ;  $\text{H}=4.32$ .

$\text{C}_9\text{H}_7\text{O}_2\text{N}$  requires  $\text{C}=61.80$ ;  $\text{H}=4.73$ ;  $\text{N}=6.01$  per cent.

*The Nitro-derivatives of 7-Hydroxycoumarin (Umbelliferone).*

**3-Nitroumbelliferone.**—A solution of umbelliferone (3.2 grams) in concentrated sulphuric acid (10 c.c.) was slowly treated at  $0^\circ$  with the nitrating mixture (4 c.c.). After one hour the liquid was poured into ice-water, when a solid was precipitated. This product was extracted twice with small quantities of boiling water, and the residue crystallised from glacial acetic acid. Golden-yellow needles, melting and decomposing at about  $245^\circ$ , were obtained:

0.1151 gave 0.2221  $\text{CO}_2$  and 0.0256  $\text{H}_2\text{O}$ .  $\text{C}=52.63$ ;  $\text{H}=2.47$ .

0.1231 " 7.8 c.c.  $\text{N}_2$  at  $24^\circ$  and 747 mm.  $\text{N}=6.98$ .

$\text{C}_9\text{H}_6\text{O}_2\text{N}$  requires  $\text{C}=52.17$ ;  $\text{H}=2.41$ ;  $\text{N}=6.76$  per cent.

**6:8-Dinitroumbelliferone.**—Umbelliferone (2 grams) was dissolved in concentrated sulphuric acid (10 c.c.), treated at  $0^\circ$  with the nitrating mixture (9 c.c.), and then warmed gently for five minutes. The cooled liquid was poured on ice, when a solid was obtained which, when crystallised from alcohol, formed yellow needles, sometimes occurring in peculiar serrated tufts, melting at  $195-196^\circ$ :

0.1863 gave 0.2630  $\text{CO}_2$  and 0.0283  $\text{H}_2\text{O}$ .  $\text{C}=43.13$ ;  $\text{H}=1.89$ .

0.1250 " 12.3 c.c.  $\text{N}_2$  at  $20^\circ$  and 758 mm.  $\text{N}=11.23$ .

$\text{C}_9\text{H}_4\text{O}_2\text{N}_2$  requires  $\text{C}=42.86$ ;  $\text{H}=1.69$ ;  $\text{N}=11.11$  per cent.

**II.—The Operations involved by the Orientation of the Nitro-derivatives of Coumarin and its Homologues.**

*The Oxidation of 3:6-Dinitrocoumarin.*—3:6-Dinitrocoumarin (1 gram) was dissolved in dilute aqueous sodium hydroxide with the aid of heat, and the resulting orange-red solution treated at  $0^\circ$  with an alkaline solution of potassium permanganate (2.5 grams). After thirty minutes, sulphurous acid was added until the liquid became clear. The excess of sulphur dioxide was removed by boiling, and the liquid then rendered alkaline with potassium hydroxide. After filtration from the precipitated manganese hydroxide, the liquid was evaporated to a small bulk, acidified with sulphuric acid, and extracted with ether. The ethereal extract, on evaporation, yielded a solid which, when crystallised from water, melted at  $223^\circ$ , and did not depress the melting point of 6-nitrosalicylic acid, prepared by nitrating salicylic acid.



**Preparation of 5-Nitro-4-methylsalicylic Acid from 6-Nitro-2-hydroxy-p-xylene.**

A solution of 6-nitro-2-hydroxy-p-xylene (1 gram) in dilute potassium hydroxide was treated at 0° with an alkaline solution of potassium permanganate (4.5 grams), and the solution then heated to boiling. Sulphurous acid was added to the liquid until a clear solution was produced, and the manganese salt then precipitated with a slight excess of potassium hydroxide. After evaporating the liquid to a small bulk, sulphuric acid was added in slight excess when a small quantity of solid separated, which, after crystallisation from water, formed white needles, melting at 212—213°. The yield was very poor:

0.1290 gave 0.2328 CO<sub>2</sub> and 0.0452 H<sub>2</sub>O. C=49.22; H=3.89.  
0.2182 „ 13.4 c.c. N<sub>2</sub> at 21° and 762 mm. N=7.01.  
C<sub>8</sub>H<sub>5</sub>O<sub>3</sub>N requires C=48.73; H=3.55; N=7.11 per cent.

**Preparation of 5-Nitro-4-methylsalicylic Acid from 6-Nitro-7-methylcoumarin, 3:6-Dinitro-7-methylcoumarin, 6-Nitro-4:7-dimethylcoumarin, and 3:6-Dinitro-4:7-dimethylcoumarin.**

The oxidation of each of the above compounds was carried out in the same manner. One gram of the substance was dissolved in dilute potassium hydroxide, the liquid being boiled when necessary. The resulting solution was treated at 0° with the calculated quantity of potassium permanganate in alkaline solution, and the liquid heated to boiling, sulphurous acid being then added until a clear solution was obtained, after which the manganese salt was precipitated with a slight excess of potassium hydroxide. The filtered solution was then evaporated to a small bulk, and acidified with sulphuric acid, when fine white needles were obtained, which, after crystallisation from water, melted at 212—213°. The product was in each case shown to be identical with the 5-nitro-4-methylsalicylic acid prepared in the preceding experiment, by the method of mixed melting points. The yield was best when the nitro-derivatives of 7-methylcoumarin were employed.

**Preparation of 3:6-Dinitro-4:5-dimethylsalicylic Acid from 5:8-Dinitro-6:7-dimethylcoumarin.**

A solution of 5:8-dinitro-6:7-dimethylcoumarin (1 gram) in dilute potassium hydroxide was treated at 0° with an alkaline solution of potassium permanganate (2.5 grams). Sulphurous acid was then added until the liquid became clear, when from the cooled

Exhaustive supply of white needles was obtained, which, when crystallized from water, melted and decomposed at about 245°:

0.1148 gave 0.1744  $\text{CO}_2$  and 0.0360  $\text{H}_2\text{O}$ .  $\text{C}=40.79$ ;  $\text{H}=3.68$ .

0.0941 " 8.7 c.c.  $\text{N}_2$  at 20° and 767 mm.  $\text{N}=10.67$ .

$\text{C}_9\text{H}_7\text{O}_2\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires  $\text{C}=40.75$ ;  $\text{H}=3.40$ ;  $\text{N}=10.57$  per cent.

*Preparation of 5-Hydroxy-4: 6: 8-trimethylcoumarin from  
5-Nitro-4: 6: 8-trimethylcoumarin.*

5-Amino-4: 6: 8-trimethylcoumarin. — 5-Nitro-4: 6: 8-trimethylcoumarin (5 grams) was mixed with dilute acetic acid (100 c.c.), and treated gradually with iron filings (5 grams). After boiling for one hour, the liquid was cooled, and the solid which separated was collected. Repeated extraction of the residue with alcohol yielded an abundant crop of yellow needles, melting at 212°:

0.1048 gave 0.2726  $\text{CO}_2$  and 0.0394  $\text{H}_2\text{O}$ .  $\text{C}=70.93$ ;  $\text{H}=6.30$ .

0.0694 " 10.4 c.c.  $\text{N}_2$  at 19° and 750 mm.  $\text{N}=6.68$ .

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C}=70.94$ ;  $\text{H}=6.40$ ;  $\text{N}=6.90$  per cent.

5-Hydroxy-4: 6: 8-trimethylcoumarin. — 5-Amino-4: 6: 8-trimethylcoumarin (1.3 grams) was warmed with concentrated hydrochloric acid (6 c.c.), a white hydrochloride being formed, which, on the addition of water (50 c.c.), underwent hydrolysis, and yielded the yellow amine in a finely divided condition. A solution of sodium nitrite (0.5 gram) was added to the cooled liquid, which was then slowly heated. The liquid gradually became clear, and then effervesced and deposited a white product. After boiling for ten minutes, the solid was collected and crystallized from alcohol, when it formed small, white, ill-defined crystals, melting at 246°:

0.1027 gave 0.2654  $\text{CO}_2$  and 0.0570  $\text{H}_2\text{O}$ .  $\text{C}=70.46$ ;  $\text{H}=6.16$ .

$\text{C}_{12}\text{H}_{12}\text{O}_2$  requires  $\text{C}=70.59$ ;  $\text{H}=5.88$  per cent.

*Preparation of 5-Hydroxy-4: 6: 8-trimethylcoumarin from  
2: 4-Dimethylresorcinol.*

2: 4-Dimethylresorcinol (0.6 gram) was mixed with ethyl acetate (0.5 gram), and concentrated sulphuric acid (2 c.c.) then added, the temperature being below 20°. After twenty hours the liquid was poured into ice-water, when a white solid was obtained, which, after crystallization from alcohol, melted at 246°, and was shown, by the method of mixed melting points, to be identical with the product obtained in the preceding experiment.

*Synthesis of 5-Nitro-6:7-dimethylsalicylic acid and 5-Nitro-6:7-dimethylsalicylic acid.*

*4:5-Dimethylsalicylaldehyde and 5:6-Dimethylsalicylaldehyde.*—Xylenol (20 grams) was dissolved in a solution of sodium hydroxide (44 grams) in water (130 c.c.), and the resulting liquid heated to 60° under reflux. Chloroform (35 grams) was added in small quantities, and the solution heated to boiling for three hours, after which the liquid was acidified with sulphuric acid and distilled in a current of steam. The distillate, which contained a heavy oil, was extracted twice with ether, and the ethereal solution shaken for some time with aqueous sodium hydrogen sulphite, when white, flaky crystals were produced, which were collected, washed with ether, and decomposed by warming with dilute sulphuric acid. The acid solution was extracted with ether, and the extract evaporated to dryness, a white, crystalline mass being thus obtained. This product was dissolved in petroleum (b. p. 40–60°), and the solution left to crystallise, when two kinds of crystals were apparent, namely, yellow, spiky needles, and pink, flaky clusters. The crystals were separated mechanically, and separately crystallised several times from light petroleum, when white, pearly plates of 4:5-dimethylsalicylaldehyde, melting at 71°, and almost white, spiky needles of 5:6-dimethylsalicylaldehyde, melting at 72°, were obtained.

*4:5-Dimethylsalicylaldehyde.*

0.1111 gave 0.2927 CO<sub>2</sub> and 0.0705 H<sub>2</sub>O. C=71.84; H=7.03.

*5:6-Dimethylsalicylaldehyde.*

0.1030 gave 0.2711 CO<sub>2</sub> and 0.0641 H<sub>2</sub>O. C=71.78; H=6.31.

C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> requires C=72.00; H=6.67 per cent.

*Oxidation of 4:5-Dimethylsalicylaldehyde.*—About equal parts of sodium hydroxide and potassium hydroxide were heated together with a little water in a nickel crucible to 180°, and 4:5-dimethylsalicylaldehyde was shaken in little at a time, hydrogen escaping after each addition. The fusion was cooled, dissolved in water, the solution filtered, acidified with dilute sulphuric acid, and finally extracted with ether. On evaporation, the extract yielded a white solid, which, after crystallisation from very dilute alcohol, formed warty masses, which softened at 180°, and melted at 195–199°. This product was shown to be identical with 4:5-dimethylsalicylic acid obtained by oxidising *p*-cumenol by the method of mixed melting.

*Oxidation of 5:6-Dimethylsalicylaldehyde.*—This operation, car-

...crystallised from dilute alcohol in white needles, melting at 143—145°.

01045 gave 0.2334  $\text{CO}_2$  and 0.0643  $\text{H}_2\text{O}$ .  $\text{C} = 64.78$ ;  $\text{H} = 5.11$ .

$\text{C}_9\text{H}_8\text{O}_4$  requires  $\text{C} = 65.06$ ;  $\text{H} = 6.02$  per cent.

3-Nitro-4:5-dimethylsalicylaldehyde. — A solution of 4:5-dimethylsalicylaldehyde (1 gram) in glacial acetic acid (10 c.c.) was treated with nitric acid (0.5 c.c.) (D 1.4) below 20°. After one hour the solution was poured into ice-water, when a solid was obtained which crystallised from alcohol in white needles, melting at 143—147°.

01674 gave 11.0 c.c.  $\text{N}_2$  at 23° and 764 mm.  $\text{N} = 7.45$ .

$\text{C}_9\text{H}_8\text{O}_4\text{N}$  requires  $\text{N} = 7.18$  per cent.

3-Nitro-5:6-dimethylsalicylaldehyde was obtained by nitrating 5:6-dimethylsalicylaldehyde in the manner described in the preceding experiment. The product was readily soluble in alcohol, and crystallised from this solvent in deep yellow needles, melting at 86—87°.

01357 gave 9.0 c.c.  $\text{N}_2$  at 21° and 763 mm.  $\text{N} = 7.42$ .

$\text{C}_9\text{H}_8\text{O}_4\text{N}$  requires  $\text{N} = 7.18$  per cent.

8-Nitro-6:7-dimethylcoumarin. — 3-Nitro-4:5-dimethylsalicylaldehyde (1 gram), anhydrous sodium acetate (1 gram), and acetic anhydride (1.5 grams) were heated together for three hours to 160—170°. The cooled product was extracted from 50 per cent. acetic acid, from which solvent almost white needles, melting at 130—134°, were obtained:

00914 gave 5.1 c.c.  $\text{N}_2$  at 15° and 760 mm.  $\text{N} = 6.53$ .

$\text{C}_{11}\text{H}_8\text{O}_4\text{N}$  requires  $\text{N} = 6.39$  per cent.

8-Nitro-5:6-dimethylcoumarin was prepared from 3-nitro-5:6-dimethylsalicylaldehyde in the manner described in the preceding experiment. Almost white needles, melting at 191—192°, were obtained:

01245 gave 7.1 c.c.  $\text{N}_2$  at 20° and 767 mm.  $\text{N} = 6.58$ .

$\text{C}_{11}\text{H}_8\text{O}_4\text{N}$  requires  $\text{N} = 6.39$  per cent.

#### Synthesis of 8-Nitro-7-methylcoumarin.

3-Nitro-4-methylsalicylaldehyde. — 4-Methylsalicylaldehyde (2 grams) was dissolved in glacial acetic acid (20 c.c.), and treated with nitric acid (0.7 c.c.) (D 1.5) below 20°. After twenty minutes the liquid was slowly heated to 45°, and then poured into ice-water. The precipitated solid, when crystallised from alcohol, formed yellow needles, melting at 126—127°.

0.1176 gave 3.1 c.c.  $N_2$  at 25° and 768 mm.  $N = 7.10$ .

$C_{12}H_9O_4N$  requires  $N = 7.73$  per cent.

5-Nitro-7-methylcoumarin was prepared from 3-nitro-4-methylsalicylaldehyde in exactly the same manner as 3-nitro-6-7-dimethylcoumarin was obtained from 3-nitro-4-5-dimethylsalicylaldehyde (see above). The product separated from its solution in acetic acid in white needles, melting at 165–166°:

0.1080 gave 6.8 c.c.  $N_2$  at 25° and 768 mm.  $N = 7.10$ .

$C_{12}H_9O_4N$  requires  $N = 6.83$  per cent.

### III.—The Products of the Action of Alkalies on the Nitro-substituted Coumarins.

*Preparation of 5-Nitrosalicylaldehyde from 3:6-Dinitrocoumarin.*—3:6-Dinitrocoumarin (5 grams) was dissolved in concentrated ammonia (100 c.c.), and the liquid boiled to expel excess of ammonia. The orange-red solution was cooled to 0°, and slowly treated with dilute hydrochloric acid until precipitation was complete. The solid product, after crystallisation from alcohol, melted at 128°, and was shown by the method of mixed melting points to be identical with the 5-nitrosalicylaldehyde obtained by nitrating salicylaldehyde.

The sodium salt was obtained by dissolving 3:6-dinitrocoumarin in the least possible quantity of aqueous 15 per cent. sodium hydroxide, and then cooling the solution. Yellow needles were obtained:

0.2987 gave 0.1110  $Na_2SO_4$ .  $Na = 12.03$ .

$C_7H_5O_4NNa$  requires  $Na = 12.17$  per cent.

*Preparation of 5-Nitro-4-methylsalicylaldehyde from 3:6-Dinitro-7-methylcoumarin.*—3:6-Dinitro-7-methylcoumarin was dissolved in concentrated ammonia with the aid of heat, and the resulting orange-red solution acidified with hydrochloric acid, as in the preceding experiment. The product separated from its alcoholic solution in yellow needles, melting at 144–145°:

0.1051 gave 0.2030  $CO_2$  and 0.0400  $H_2O$ .  $C = 52.67$ ;  $H = 4.22$ .

0.1032 „ 7.4 c.c.  $N_2$  at 23° and 749 mm.  $N = 8.00$ .

$C_8H_7O_4N$  requires  $C = 53.04$ ;  $H = 3.87$ ;  $N = 7.73$  per cent.

The crism, prepared in the usual way, crystallised from alcohol in yellow needles, melting, sometimes with decomposition, at 207–208°:

0.1323 gave 15.2 c.c.  $N_2$  at 19° and 760 mm.  $N = 14.29$ .

$C_{12}H_9O_4N_2$  requires  $N = 14.29$  per cent.

The  $\alpha$ -methylketone crystallized from dilute acetic acid in yellowish-brown needles, melting at 201–202°.

0.1024 gave 12.5 c.c.  $N_2$  at 15° and 760 mm.  $N = 15.48$ .

$C_{14}H_{10}O_2N_2$  requires  $N = 15.50$  per cent.

*Preparation of 3:6-Dinitro-4:5-dimethylacetylaldehyde from 3:5:8-Trinitro-6:7-dimethylcoumarin.*—3:5:8-Trinitro-6:7-dimethylcoumarin (2 grams) was heated with concentrated ammonia (80 c.c.) until solution took place. The cooled orange liquid was carefully acidified with dilute hydrochloric acid, when a solid was obtained which, after crystallization from alcohol, formed yellow needles, melting at 147–148°.

0.1217 gave 0.2022  $CO_2$  and 0.0390  $H_2O$ .  $C = 45.31$ ;  $H = 3.56$ .

0.1049 „ 11.4 c.c.  $N_2$  at 20° and 742 mm.  $N = 11.90$ .

$C_{14}H_8O_2N_2$  requires  $C = 45.00$ ;  $H = 3.33$ ;  $N = 11.67$  per cent.

*Preparation of  $\alpha$ -5-Dinitro-2-hydroxy- $\alpha$ -4-dimethylstyrene from 3:6-Dinitro-4:7-dimethylcoumarin.*—Finely powdered 3:6-dinitro-4:7-dimethylcoumarin (1 gram) and a 15 per cent. solution of sodium hydroxide (30 c.c.) were boiled together for two minutes, then filtered from a small quantity of undissolved solid. The filtrate was carefully acidified below 0° with dilute hydrochloric acid, when a solid was obtained which was dried at the ordinary temperature and then extracted with benzene. The extract deposited a yellowish-brown, crystalline powder, which melted at 120–121°, and was decomposed by heating with alcohol or water:

0.1452 gave 0.2690  $CO_2$  and 0.0554  $H_2O$ .  $C = 50.52$ ;  $H = 4.24$ .

0.1475 „ 15.3 c.c.  $N_2$  at 18° and 752 mm.  $N = 11.86$ .

$C_{14}H_{10}O_2N_2$  requires  $C = 50.42$ ;  $H = 4.20$ ;  $N = 11.76$  per cent.

The sodium salt was prepared by dissolving 3:6-dinitro-4:7-dimethylcoumarin in the smallest possible quantity of 15 per cent. aqueous sodium hydroxide, the liquid being boiled for not longer than two minutes. The hot solution was filtered through glass wool and cooled to 0°, when a small quantity of yellow needles was deposited, which were washed on a filter with absolute alcohol. The salt is very soluble in water, and deflagrates violently when heated:

0.3129 gave 0.1543  $Na_2SO_4$ .  $Na = 15.95$ .

$C_{14}H_8O_2N_2Na_2$  requires  $Na = 16.31$  per cent.

*Preparation of 6:8-Dinitrocoumarinic Acid from 6:8-Dinitrocoumarin.*—6:8-Dinitrocoumarin was dissolved in 15 per cent. sodium hydroxide with the aid of heat. The clear red liquid was cooled to 0°, and carefully acidified with dilute hydrochloric acid. The yellow precipitate was collected and dried at the ordinary temperature, when it melted at about 153° with a copious evolution

Yellow needles were obtained from the mother liquor. The substance is rapidly converted into 8-nitro-7-hydroxycoumarin when its solution in water or alcohol is heated:

0.1562 gave 0.2410  $\text{CO}_2$  and 0.0371  $\text{H}_2\text{O}$ .  $\text{C}=42.06$ ;  $\text{H}=3.24$ .

0.1003 " 10.0 c.c.  $\text{N}_2$  at 19° and 760 mm.  $\text{N}=11.46$ .

$\text{C}_9\text{H}_5\text{O}_4\text{N}_2$  requires  $\text{C}=42.52$ ;  $\text{H}=3.36$ ;  $\text{N}=11.02$  per cent.

*Preparation of 8-Nitro-7-hydroxycoumarinic Acid from 8-Nitro-7-Hydroxycoumarin.*—8-Nitro-7-hydroxycoumarin was dissolved in aqueous 15 per cent. sodium hydroxide, the temperature being raised to 30° for one minute. The red liquid was acidified at 0° with dilute hydrochloric acid, when it deposited a fine scarlet powder, which was dried at the ordinary temperature, and crystallised from dry ether. The scarlet needles which separated gradually became yellow when heated, and finally melted and decomposed at 240–245°. The yellow product was shown to be 8-nitro-7-hydroxycoumarin by the method of mixed melting points. The scarlet compound was also found to be completely converted into the yellow parent coumarin when heated for some time to 150°:

0.1464 gave 0.2562  $\text{CO}_2$  and 0.0456  $\text{H}_2\text{O}$ .  $\text{C}=47.73$ ;  $\text{H}=3.46$ .

0.1624 " 8.9 c.c.  $\text{N}_2$  at 23° and 763 mm.  $\text{N}=6.20$ .

$\text{C}_9\text{H}_5\text{O}_4\text{N}$  requires  $\text{C}=48.00$ ;  $\text{H}=3.11$ ;  $\text{N}=6.22$  per cent.

The author desires to express his thanks to the Chemical Society for a grant which has in part defrayed the expense incurred during this investigation.

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### CXXIX.—*Estimation of Sodium and Caesium as Bismuthinitrites. Part I. Estimation of Sodium.*

By WALTER CRAVEN BALL.

IN a recent paper (Trans., 1909, 95, 2126) the author showed that sodium salts produce a precipitate of sodium caesium bismuthinitrite,  $9\text{CaNO}_2 \cdot 8\text{NaNO}_2 \cdot 5\text{Bi}(\text{NO}_2)_3$ , when added to a solution of potassium nitrite containing bismuth nitrate and caesium nitrate. No corresponding potassium salt appears to exist, and the sodium salt, precipitated from solutions containing several thousand times as much potassium as sodium, is free from the former metal.

The following paper, which dealt primarily with the estimation of sodium, included also the results of a few estimations of sodium in sodium caesium bismuthinitrite, which indicated that the method might prove to be an accurate one. As will be seen from the appended tables of results (tables A and B, pp. 1413, 1414), this is the case, provided that the reagent is made up as described, and that the precautions mentioned with regard to collecting and washing the precipitate are observed.

A great advantage of the method is that none of the metals commonly associated with sodium in analysis, such as calcium, magnesium, lithium, and ammonium, interfere, at least when present in the amounts used in these experiments, and, as mentioned above, traces of sodium may be estimated in potassium salts. Another advantage is that the precipitate contains only 3.675 per cent. of sodium, so that 1 milligram of the metal yields 27.2 milligrams of precipitate.

On the other hand, chlorides should not be present in greater concentration than  $N/5$ , or bismuth oxychloride may separate. Phosphates, if present in more than traces, must be removed.\*

Iodides interfere, as also do citrates and the salts of some other hydroxy-acids. Sulphates, nitrates, nitrites, acetates, and formates do not interfere. Most of the heavy metals, particularly silver, must be absent. The method is particularly applicable to the estimation of small amounts of sodium in mixtures such as sea-water; for example, the sodium in 0.2 c.c. of sea-water was determined directly with fair accuracy. It may therefore be found useful in the analysis of soils, etc., and in physiological chemistry.

The estimation is not a costly one, and the caesium, the only expensive ingredient, may be easily obtained pure from the residues by the addition of silver nitrate, which precipitates a very insoluble salt, silver caesium bismuthinitrite.† This, on heating and subsequent extraction with water, yields a pure caesium salt.

*Preparation of the Reagent.*—This is made by adding bismuth nitrate and caesium nitrate to a solution of pure potassium nitrite. As all the samples of this salt were very impure, generally containing much sodium, and as it cannot be purified to any extent by recrystallisation, the author prepared it by passing nitrous fumes into a concentrated solution of potassium carbonate, which salt can be bought almost free from sodium.

Thirty grams of the pure nitrite; are dissolved in a little water,

\* This may be done by warming to  $100^\circ$  with a solution of potassium nitrite (pure) to which bismuth nitrate has been added.

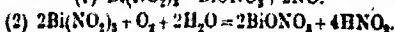
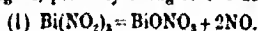
† If excess of silver nitrate be added, this will contain also silver potassium bismuthinitrite, which may be removed by reprecipitation.

‡ This can now be obtained, almost free from sodium, from Messrs. Messrs.



and to this are added 3 grams of bismuth nitrate dissolved in a little dilute nitric acid (the solution used contained 30 grams of the crystallized salt made up to 50 c.c. with approximately 2 N-nitric acid; 3.75 c.c. of this contained 3 grams of the nitrate). Should the resulting yellow liquid be turbid, which may occur if the nitrite contains free alkali, dilute nitric acid must be added until it is clear. Then 16 c.c. of a 10 per cent. solution of cesium nitrate are added, and the volume made up to 100 c.c. with water, or, if turbid, with water and a little nitric acid.

Even when made from the purest reagents obtainable, this liquid will slowly deposit a small, yellow precipitate of sodium cesium bismuthinitrite. The liquid should be kept for two days, and then filtered from the precipitate, when it is then practically free from sodium. If exposed to the air, a white scum appears on the surface of the reagent, probably owing to two different reactions:



It may be kept for some weeks in a stopped cylinder provided with a Bunsen valve, especially if protected from the air by coal gas or a layer of paraffin.

The proportion of potassium nitrite may be lowered to 25 or 30 grams per 100 c.c., but such a reagent does not keep so well, and appears to be less trustworthy. The amount of bismuth nitrate may be increased to 6 grams or more, but again this reagent is much less stable, although it causes a more rapid precipitation; less than 3 grams of bismuth nitrate per 100 c.c. must not be used. Addition of cesium nitrate beyond 1.6 to 1.8 grams per 100 c.c. of reagent causes the weight of precipitate to be too large. More than 2 grams of cesium nitrate per 100 c.c. produces a precipitate of hexagonal plates of cesium bismuthinitrite, and it is possible that an admixture of this compound is the cause of the too high weight of precipitate obtained when the reagent contains more than 1.6 to 1.8 grams of cesium nitrate per 100 c.c.\* It is found also that the precipitate of cesium bismuthinitrite is formed with lower concentrations of cesium when the concentration of potassium nitrite is also lowered; thus a reagent containing 30 grams of potassium nitrite and 2 grams of cesium nitrate per 100 c.c. deposited no hexagonal plates.

\* These precipitates, however, when examined with the microscope, appear to be free from the hexagonal crystals of cesium bismuthinitrite and to be homogeneous. Another possible explanation is that various sodium cesium bismuthinitrites exist in which the atomic ratio of cesium to sodium varies from 3:2, as in the formulae  $\text{CsNO}_2 \cdot 3\text{NaNO}_2 \cdot 3\text{Bi}(\text{NO}_2)_3$  to 2:1, as in the formula  $2\text{CsNO}_2 \cdot \text{NaNO}_2 \cdot \text{Bi}(\text{NO}_2)_3$ . The ratio of cesium to sodium was determined in some of these precipitates, and appeared to approach, but never quite reached, the higher value. The point is a difficult one to determine.

whereas one containing 15 grams of potassium nitrite and 1 gram of cesium nitrate gave more than 1 gram of cesium bismuthinitride.

The reagents should therefore be made up as described. If a reagent giving a more rapid precipitation is required, the author's experiments indicate that this might perhaps be effected by using a greater concentration of cesium, and finding experimentally a factor for converting the weight of precipitate into weight of sodium.

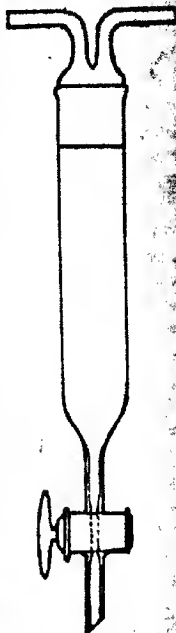
Of the three metals, sodium, cesium, and bismuth, any one may probably be completely precipitated by the presence of a large excess of the other two.

One c.c. of the above reagent will precipitate 0.5 to 0.7 milligram of sodium. The reagent thus prepared may be used for the detection of sodium, instead of that described in the former paper, as it is more stable, and almost equally delicate.

#### Method of Precipitation.

The reagent must be kept as much as possible from contact with the air, and therefore the precipitation must be conducted in a vessel filled with coal gas or other inert gas. The author uses a cylindrical tapped funnel, as illustrated, provided with a stopper containing two tubes for the replacement of air by coal gas. This stopper may be of rubber, but glass is better, as the rubber is attacked by the nitrous fumes. These cylinders may be roughly graduated so that various quantities of the reagent may be measured into them. Fairly accurate results may also be obtained by dispensing with this apparatus and using a conical beaker, finally washing out the precipitate with the mother liquor; but unless this is very carefully done, the results are not so accurate.

Suppose that a quantity of 10 milligrams of sodium is to be estimated. In this case 20 to 25 c.c. of the reagent are placed in a cylinder (capacity about 50 c.c.), 1 c.c. of dilute nitric acid (about 2*N*) added, and the sodium salt, dissolved in 5 c.c. or less of water, is added. The mixture is well stirred (a glass rod expanded at the end answers best), coal gas passed into the cylinder for a few seconds, and the tubes closed, one by a rubber cap, the other by a Bunson valve.



... in  
... and will collect in the lower part of the cylinder.  
... twenty-four to forty-eight hours (twenty-four hours being  
... results which are generally a little low, but it will be seen  
... the appended figures that the difference is very small. The  
... precipitate is stirred with a stout wire, so that it will easily pass  
... through the tap. This is then opened, and the precipitate and  
... liquid allowed to run into a small Gooch crucible, with a dirty  
... black asbestos felt. The liquid should be run into the Gooch  
... crucible at such a rate that the precipitate is covered with the  
... liquid during the filtration. The filtrate is received in a clean  
... filter flask, poured back as quickly as possible into the cylinder,  
... any precipitate remaining on the walls of the cylinder stirred into  
... the liquid with a rubber-tipped glass rod, and the filtration repeated.

The essential point is the complete transference of the precipitate  
from the cylinder to the crucible, with the least possible exposure  
to the air, and this requires some care to accomplish. The pro-  
duction of a small amount of scum on the sides of the cylinder  
during the second filtration has no perceptible effect on the  
estimation. Unless the first filtrate is not clear, it is not necessary  
again to filter the whole of it, but a little will be required to wash  
any precipitate adhering to the sides of the cylinder.

The precipitate is then washed rapidly by suction with 5 c.c. of  
a mixture of equal volumes of acetone and water (10 c.c. if the  
precipitate be a large one) contained in a small wash bottle, and  
then with pure acetone. The washing liquid must be directed  
against the sides of the crucible, in order to wash down any  
adhering traces of the reagent. Finally, the suction is stopped,  
some acetone is put into the crucible, and suction again started  
slowly. The precipitate is then dried at  $100^{\circ}$  (fifteen minutes  
usually), and weighed.

An alternative method is to use 5 to 10 c.c. of a 5 per cent.  
solution of pure potassium nitrite (containing no free alkali), and  
then acetone as above.

Experiments were made with many other washing agents; none  
completely removed the mother-liquor without at the same time  
dissolving a little of the precipitate. The two mentioned yield  
the best results; a first washing with 60 to 70 per cent. acetone,  
with 5 per cent. sodium nitrite was generally less satisfactory.  
Acetone itself has no action on the precipitate.

For each 5 c.c. of 50 per cent. acetone used, 0.07 milligram may  
be added to the amount of sodium found, and for each 5 c.c. of  
5 per cent. potassium nitrite about 0.1 milligram, to correct for  
precipitate dissolved. The results of some deter-

TABLE A.—Results of Sodium Estimations, using 50 per cent. Acetone or 5 per cent. Potassium Nitrate, and subsequently Pure Acetone, to wash the Precipitate.

No. of experiment.	Sodium salt used.	C.c. of salt solution.	C.c. of reagent used.	Time elapsed for precipitation, hours.	Sodium taken, gram.	Sodium found, gram.	Sodium found, corrected for loss in washing, gram.	Method of washing, and remarks.
1	Nitrate	5	40	24	0.0217	0.0219	0.0250	50 per cent. acetone, then acetone
2	"	2	20	21	0.0099	0.0097	0.0097	" " "
3	"	2	20	24	0.0079	0.0077	0.0077	" " "
4	"	2	20	24	0.0079	0.0079	0.0080	" " "
5	"	2	20	45	0.0079	0.0053	—	" " "
6	"	4	25	48	0.0157	0.0152	0.0153	This result, decidedly too high, may be due to incomplete washing
7	"	2	20	72	0.0099	0.0095	0.0099	50 per cent. acetone, then acetone
8	"	2	20	84	0.0079	0.0078	0.0079	" " "
9	"	2	20	86	0.0079	0.0078	0.0079	" " "
10	Acetate	2	20	24	0.0086	0.0087	0.0088	" " "
11	"	2	40	48	0.0091	0.0097	0.0099	" " "
12	"	10	90	45	0.0159	0.0157	0.0159	" " "
13	"	2	20	70	0.0086	0.0086	0.0086	The quantity of dilute nitric acid added was, in this experiment, larger than usual
14	"	1	10	72	0.0043	0.0040	0.0041	50 per cent. acetone, then acetone
15	Chloride	2	20	72	0.0086	0.0087	0.0088	" " "
16	"	2	20	72	0.0083	0.0081	0.0082	" " "
17	"	2	20	72	0.0054	0.0054	0.0055	5 per cent. potassium nitrate, then acetone
18	Sulphate	5	20	25	0.0130	0.0127	0.0131	10 per cent. potassium nitrate, then acetone

A number of estimations, in which the precipitates were washed with solutions of sodium nitrate of 1 to 5 per cent. strength, are not included, as the results, although they agreed fairly well with the above, were not so concordant. As solutions of sodium nitrate have little action on the precipitate, it was thought that they would tend to remove all mother-liquor from the precipitate, and that, in the short time required for the dilution, no appreciable error would be caused by further precipitate formed by the sodium nitrate and the small quantity of mother-liquor adhering to the precipitate. The method was, however, given up as unsatisfactory.

estimations are given in tables A and B, experiments 1 and 2. The other washing liquids than those recommended were used, having been omitted, as they did not give such concordant results.

After a little experience, very concordant values may be obtained. For example, three determinations, similar in all respects, of equal quantity of sodium gave:

- (1) Precipitate = 0.2069 gram = 0.00720 gram Na.  
 (2) " " = 0.2062 " = 0.00736 "  
 (3) " " = 0.2063 " = 0.00749 "

TABLE B.—Estimations of Sodium in Presence of a Mixture of Potassium Sulphate, Magnesium Nitrate, Ammonium Nitrate, Lithium Nitrate, Calcium Chloride, and Rubidium Chloride.

No. of experiment	Sodium salt used.	Substances added, gram.	Time allowed for precipitation, hours.	Sodium taken, gram.	Sodium found, gram.	Sodium found, corrected for loss in washing, gram.
1	Nitrate	0.040 potassium sulphate 0.024 magnesium nitrate 0.008 ammonium " " 0.004 lithium " " 0.004 rubidium chloride 0.004 calcium " "	48	0.0058	0.0060	0.0060
2	"	As in experiment 1	48	0.0060	0.0057	0.0057
3	"	As in experiments 1 and 2	72	0.0058	0.0059	0.0059
4	"	0.020 potassium sulphate 0.012 magnesium nitrate 0.004 ammonium " " 0.002 lithium " " 0.002 rubidium chloride 0.002 calcium " "	72	0.0079	0.0075	0.0076

Sea Water.—Some sea-water was diluted to one-fifth, and the sodium estimated in 2 c.c. Calculated as sodium chloride, the results of three estimations were:

2.6	grams of sodium chloride per 100 grams of sea-water.
2.4	" " " " " "
2.5	" " " " " "

The specific gravity of the sample was 1.028, and the total amount of solids 3.393 grams per 100 grams of sea-water. (Average values for similar sea-water are 2.64 grams sodium chloride per 100 grams; specific gravity, 1.026; total solids, 3.39 grams per 100 grams.)

Part of the cost of this investigation was defrayed by a grant from the Chemical Society, for which the author desires to express his thanks.

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## CXXX.—Carthamine. Part I.

By TOKUMI KANETAKA and ARTHUR GEORGE PERKIN.

**Safflower**, the *Carthamus tinctorius*, at one time a most important red dyestuff, on the advent of safranine quickly fell into disuse throughout Europe, but nevertheless large quantities are still cultivated, more especially in India, and employed for dyeing and pigment manufacture. The red colouring matter, carthamine, is present in the flowers to the extent of 0.3 to 0.6 per cent. (Salvetat, *Ann. Chem. Phys.*, 1849, [iii], 25, 337), together with a very large amount of a soluble yellow substance, which is useless and even harmful in the dyeing operation. Although carthamine is specially interesting on account of its substantive dyeing properties, it appears to have received but little attention, and this is probably due to the tedious and expensive character of the peculiar operations which are necessary for its isolation from the plant. For this purpose it is usual to extract the flowers, which have been previously washed with water in order to remove the yellow substance, with dilute sodium carbonate solution. If the alkaline extract be now acidified with citric or tartaric acids, the carthamine is precipitated in so finely divided a condition that it cannot be successfully collected, and to obviate this difficulty cotton or flax is dyed with the colouring matter by immersion in the alkaline liquid, followed by a subsequent acidification of the dye-bath. The carthamine is now removed from the dyed cotton by means of sodium carbonate solution, and is deposited from this extract by means of an organic acid in a purer and more granular form. The crude material employed in this investigation was procured from Kyoto in Japan, a country in which it finds considerable employment as a cosmetic. For its preparation the safflower, which is imported both from China and India, is subjected to a process very similar to that outlined above, the alkali being supplied by plant-ash extract, and the organic acid from the juice of the Japanese plum. Considerable experience appears to be necessary in neutralising the alkaline extract of the plant, and also of the dyed cotton, for, should this be carried beyond a certain point, a brown impurity is subsequently deposited, which causes a considerable deterioration of the brilliancy of the colouring matter. The yield of dyestuff varies according to the quality of the plant, but according to figures given by the Japanese maker, 80 lbs. of the dried flowers usually yield about 285 grams of crude carthamine.

Samples described as carthamine were also procured by purchase

from the Continent, but these were useless for our purpose, and contained little or none of the colouring matter. Although no doubt originally derived from safflower, the dye had evidently been decomposed during the extraction process; moreover, it would appear that some novel method of isolation had been attempted, for on incineration it yielded 15.7 per cent. of ash, mainly calcium carbonate, whereas the ash of the Japanese product (12.8 per cent.) consisted almost entirely of potassium carbonate.

Preisser, the first to investigate carthamine (*J. pr. Chem.*, 1844, [i], 32, 142), describes this substance as colourless needles, which, by air oxidation in the presence of alkali, were converted into carthamein, the true colouring matter. Schlieper (*Annalen*, 1846, 58, 337), however, considered that Preisser's statements were absolutely incorrect, and he isolated carthamine in the form of green, iridescent, red crusts, or as a granular, greenish-red powder, to which he assigned the formula  $C_{11}H_{11}O_7$ . When digested with boiling alcohol, it was converted into a yellow compound having the composition  $C_{11}H_{11}O_6$ . According to Malin (*Annalen*, 1840, 36, 117), carthamine gives *p*-hydroxybenzoic acid when digested with boiling potassium hydroxide solution.

Much more recently Radcliffe (*J. Soc. Dyers*, 1897, 13, 158), by extracting an air-dried commercial paste extract of safflower with methyl alcohol, subsequently evaporating the solution, and adding hot water, obtained a product crystallising in red, iridescent needles melting at 168–169° (provisional), which, when exposed to sunlight, changed to a red powder. A study of the absorption spectra of solutions of this substance, and an account of its general properties are described in his paper, but he reserved analytical details for a later communication.

Although carthamine has proved to be somewhat more stable than was anticipated, the ease with which it undergoes alteration in the presence of most reagents, together with its expensive nature, has shown that the investigation of this compound is an extremely difficult problem. The communication of the somewhat meagre results given below, and which can only be regarded as of a preliminary nature, is rendered necessary by the fact that our joint work has now to cease.

#### EXPERIMENTAL

In order to repeat Radcliffe's experiments (*loc. cit.*), some portion of the Safflower extract was procured from Japan in the condition of a bright red paste, but the main bulk consisted of the dried substance in the form of green, iridescent fragments still attached to the silken material, on which it had evidently been drained.

The paste, after drying at the ordinary temperature, was exhausted in the finely divided condition with methyl alcohol, and after concentration the solution was treated with hot water. On standing, fine, hair-like needles separated out, which, when collected and dried, formed about 6 per cent. of the original material, and evidently corresponded with Radcliffe's preparation.\* Examination showed that not only was the undissolved substance, which still contained a large quantity of the colouring matter, most sparingly soluble in hot methyl alcohol, but that the dried crystals were also but little attacked by this solvent, so that a recrystallisation in this manner was difficult to carry out. It accordingly seems probable that in the colloidal condition carthamine is somewhat readily dissolved by boiling alcohol, but otherwise it is not, and bearing in mind Schlieper's statement (*loc. cit.*), that carthamine is decomposed by long boiling with alcohol, this method of purification, which involved a long digestion with very large quantities of the solvent, was abandoned. Radcliffe found that when the safflower extract he employed was evaporated to dryness on the water-bath, the heating destroyed the colouring matter, but as experiments with the Japanese product did not confirm this point, it is evident that in the former case some special impurity of the extract must have been responsible for this change.

In order to devise a more ready method for the purification of the crude material, repeated trials were carried out, and ultimately the use of pyridine was adopted. In this liquid, carthamine somewhat readily dissolves, but owing to the sensibility of the colouring matter, it is preferable to conduct the extraction process and the subsequent operations at as low a temperature as possible. Forty grams of the finely powdered material were treated with 400 c.c. of pyridine (Kahlbaum's I) on the water-bath for about fifteen minutes, and the undissolved residue treated in a similar manner, first with 200 c.c. of pyridine, and finally with 100 c.c. of the same solvent, or until the filtrate was no longer red coloured. The united pyridine extracts were now concentrated under diminished pressure (40 mm.) at 60–65° to a small volume, and warm water was then added until a faint turbidity occurred. On keeping, a beautiful semi-solid, crystalline mass was obtained, and this was collected and washed with a little water. The product thus obtained had a very pure appearance, and averaged, when dry, 22.5 grams, or a yield of 56 per cent., whereas the insoluble residue was 10.5 grams, or 26 per cent. of the original material.

Examination showed that the crystalline carthamine contained,

\* These crystals contained a large amount of mineral matter, apparently in combination with the carthamine.



not only a trace of mineral matter, but some quantity of anhydrous wax, and to remove the latter the crystals were extracted in a Soxhlet apparatus, first with chloroform and then with ether. As carthamine gradually suffers alteration in the presence of hot dilute mineral acid, the inorganic matter could not be well removed by such a treatment, but experiment indicated that this could be effected by repeated crystallisation from pyridine, and washing with water. Unfortunately, however, it is difficult to recover satisfactorily the colouring matter from the pyridine mother liquors, and as in each operation but 60 per cent. of the dissolved substance separates on cooling, the loss of the very expensive carthamine is serious, and the yield of the chemically pure compound does not average more than 25 to 30 per cent. of the original dry extract.

When purified in this manner, carthamine contains pyridine of crystallisation, which is not removed by washing the crystals with ether or benzene. For analysis, it was dried at  $125^{\circ}$  or  $160^{\circ}$ , and when anhydrous was exceedingly hygroscopic, a fact which rendered the weighing operations somewhat difficult:

Found, C=58.16, 58.47, 58.33, 57.91; H=4.87, 4.23, 4.83, 4.90  
 $C_{14}H_{11}O_7$  (Schlieper, *loc. cit.*) requires C=57.14; H=4.76 per cent.

$C_{15}H_{11}O_7$  requires C=58.82; H=4.57 per cent.

$C_{15}H_{11}O_{12}$  " C=58.14; H=4.65 "

As obtained in this way, carthamine consists of bright scarlet coloured, prismatic needles, which melt and decompose at about  $228-230^{\circ}$ , a point which is considerably higher than that given provisionally by Radcliffe (*loc. cit.*). According to Schlieper, and also to Radcliffe, carthamine is freely soluble in cold alcohol, and this is curious because the chemically pure substance, although giving with ethyl and methyl alcohols a coloured solution in the cold, was only sparingly soluble in these liquids, even on boiling. On the other hand, it is somewhat more readily dissolved by methylated spirit, but is almost insoluble in acetone, in which again Radcliffe states it is freely soluble. Carthamine dissolves in dilute alkali hydroxides, sodium carbonate, and ammonia with an orange colour, and on addition of acid is reprecipitated unchanged, but the product exhibits the somewhat unfortunate characteristic of this colouring matter that when collected it cannot be washed with water without passing through the paper. If carthamine is, however, dissolved in a little strong ammonia, the solution treated with glacial acetic acid, and then with its own volume of alcohol and boiled, the colouring matter is thus deposited in a beautifully crystalline condition. Cold alkaline solutions of the substance suffer oxidation on exposure to the air, with the formation of a brown liquid, from which acids throw down a black-coloured precipitate.

With *nitric acid*, carthamine forms a dull red-coloured solution, which, after heating to 100°, gives with water a violet precipitate, possessing feeble mordant dyeing properties, and is soluble in alkalis with a green coloration. Although carthamine is not perceptibly attacked by cold dilute acids, on heating an alteration occurs with formation of a dull brown precipitate, which does not appear to be susceptible to crystallisation. Hydrochloric acid (33 per cent.), in the presence of boiling acetic acid, reacts somewhat similarly to sulphuric acid, and the product is soluble in alkalis with a green tint. Alcoholic lead acetate gives with carthamine a bright scarlet precipitate soluble in water, and alcoholic ferric chloride a deep brown coloration. When examined by Zeisel's method, no trace of a methoxy-group could be obtained. As was to be expected from its behaviour with lead acetate, carthamine is devoid of affinity for mordants, but is *per se* a substantive dyestuff toward silk, wool, and cotton.

*Action of Nitric Acid.*—Nitric acid (D 1.5) dissolves carthamine with a deep orange coloration, from which water throws down a yellow precipitate. The acid liquid, when evaporated to a small bulk, on cooling solidified to a crystalline mass, which was drained on a tile, and recrystallised from water. It consisted of pale yellow leaflets, melting at 118–120°, and had all the properties of picric acid.

*Action of Fused Alkali.*—Carthamine was heated with ten times its weight of potassium hydroxide and a little water to 210–220° for about fifteen minutes. The pale brown coloured melt was dissolved in water, the solution neutralised with acid, extracted with ether, and the extract evaporated. A crystalline mass was thus obtained, which possessed a strong odour of acetic acid, and in order to isolate a phenol, if such was present, it was dissolved in a solution of sodium hydrogen carbonate, and the liquid agitated with ether. As this gave a negative result, the solution was again neutralised with acid, the substance recovered by means of ether, and purified by crystallisation from water.

It consisted of colourless needles, melting at 208–210°, and had all the properties of *p*-hydroxybenzoic acid. Malin's statement (*loc. cit.*) is thus confirmed.

*Action of Dilute Alkali.*—Experiments were now carried out on the action of boiling potassium hydroxide solutions (50 c.c.), varying in strength from 50 per cent. to 1 per cent., on carthamine (1 gram), from which it became evident how very sensitive this colouring matter is under these conditions. The solutions quickly became brownish-yellow coloured, and, on neutralisation with acid, a brown precipitate (A) separated, which varied in quantity

according to the concentration of the reagent and the length of the digestion. Thus, by heating with 50 per cent. alkali for half an hour, but a trace of this brown product was obtained, whereas with 5 per cent. alkali the yield was about 50 per cent. It was collected, the clear liquid repeatedly agitated with ether, and the ethereal extract evaporated to a small bulk. The residual solution was treated with its own volume of benzene, and slowly concentrated with the result that at first a small quantity of a resin separated, which was filtered off, and on further distillation minute crystals were deposited. These were collected and crystallised from water, in which they were very sparingly soluble, until colourless. (Found,  $C = 65.73$ ;  $H = 4.95$ .  $C_9H_6O_3$  requires  $C = 65.85$ ;  $H = 4.88$  per cent.)

It consisted of long needles, which melted at  $207-208^\circ$ , and gave with ferric chloride a brown coloration. These properties suggested that it was *p*-coumaric acid, and this was confirmed by a comparison with the synthetical product, prepared according to Eigel's directions (*Her.*, 1887, 20, 2539).

The benzene mother liquors from which the coumaric acid had separated were concentrated to a very small volume, and on keeping overnight became semi-solid, owing to the separation of crystals. These were collected, drained on porous porcelain, and crystallised from water with the aid of animal charcoal. When obtained in this way the substance melted at  $113-114^\circ$ , but as it still contained a yellow impurity it was carefully sublimed between watch glasses, and finally crystallised from water. (Found,  $C = 68.76$ ;  $H = 4.97$ .  $C_9H_6O_3$  requires  $C = 68.85$ ;  $H = 4.92$  per cent.) It now fused at  $115-117^\circ$ , gave with ferric chloride a pale violet coloration, and was identified as *p*-hydroxybenzaldehyde by comparison with the synthetical product.

The brown, resinous compound (A), also produced by the action of the alkali on carthamine, could not be crystallised, and was therefore again submitted to the action of the boiling dilute alkali. In this manner it yielded a further quantity of *p*-coumaric acid and *p*-hydroxybenzaldehyde, and it thus appears likely that no third ether soluble product can be obtained from carthamine by this reaction.

Carthamine is also decomposed when digested with strong boiling barium hydroxide solution, and there is thus produced a trace of *p*-coumaric acid and *p*-hydroxybenzaldehyde, together with a large quantity of brown, resinous substance.

*Action of Hydrogen Peroxide.* Two grams of carthamine, dissolved in 200 c.c. of 1 per cent. sodium carbonate solution, were treated with 3.8 c.c. of hydrogen peroxide (Merck's perhydrol) and the liquid kept overnight. The resulting yellow solution

was modified, repeatedly extracted with ether, and the ether evaporated. The yellow, crystalline residue was purified by crystallisation from water, in which it was very sparingly soluble, employing animal charcoal. (Found,  $C=65.73$ ;  $H=4.93$ ,  $C_{20}H_{15}O_5$  requires  $C=65.85$ ;  $H=4.88$  per cent.) It melted at  $207-208^\circ$ , and was found to consist of *p*-coumaric acid. Experiments on the oxidation of carthamine with perhydrol were also carried out in the presence of acetic acid. Addition of water caused the separation of a yellow, gelatinous precipitate, soluble in alkalis with a yellow colour, and which separated from methyl alcohol and water in an amorphous condition. The filtrate contained *p*-coumaric acid.

*Benzoylcarthamine*.—One gram of carthamine, dissolved in 15 c.c. of pyridine, was treated with 11 c.c. of benzoyl chloride in the usual manner. The next day addition of water caused the separation of a resinous mass, which was purified by adding alcohol to its solution in acetone, and repeating the same operation two or three times. Two distinct preparations were made, but up to the present attempts to crystallise this compound have failed. To be certain that it was completely benzoylated, it was submitted to the action of benzoic anhydride at  $170^\circ$  for a few minutes, and recovered by precipitation from alcohol.

Found,  $C=70.85$ ;  $H=4.41$ ;  $C=70.98$ ;  $H=4.42$ ;  $C=70.92$ ;  $H=4.35$ .

$C_{22}H_{17}O_5(C_6H_5O)_2$  requires  $C=71.38$ ;  $H=4.18$  per cent.

$C_{22}H_{17}O_5(C_6H_5O)_2$  "  $C=70.52$ ;  $H=4.21$  "

It consisted of a pale red, amorphous powder, which sintered at  $210^\circ$ , and melted and decomposed at about  $230-232^\circ$ .

Attempts to prepare a crystalline acetyl derivative\* from carthamine by Deminger's method have as yet been unsuccessful. By the action of boiling acetic anhydride, the acetylation is accompanied by decomposition, the solution rapidly darkens, and gives an indefinite amorphous compound.

On account, also, of the extreme sensitiveness of carthamine to alkali, it does not appear to be possible to methylate this colouring matter, either by means of methyl sulphate or methyl iodide, without at least some portion of the product becoming decomposed, and the result of numerous experiments indicated that this was the case. In the hope of obtaining a more satisfactory result, the action of an ethereal solution of diazomethane on carthamine was studied. The well-dried colouring matter suspended in anhydrous ether was

\* The amorphous substance thus produced gave  $C=57.95$ ,  $H=4.32$ , and agrees fairly well with  $C_{20}H_{15}O_5(C_2H_5O)_2$ , which requires  $C=57.75$ ;  $H=4.68$  per cent. Its purity was, however, doubtful.

treating with excess of this reagent, causing the evolution of gas and the gradual change of the substance from red to yellow. After keeping overnight, the product was collected, but on examination the greater bulk of the substance was found to be insoluble in all solvents, and in appearance somewhat resembled cork. By Ziesel's method the presence of methoxy-groups could not be detected. A repetition experiment gave the same result, and it was evident that in this case the behaviour of the diazomethane is abnormal. In addition to this product, a small quantity of yellow, amorphous substance was also formed, which was soluble in alcohol, gave on analysis OMe 25.7 per cent., and possibly contained a trimethyl ether, but the yield was not sufficiently good to permit of its further examination.

A study was now made of the oxidation of the crude methylation product of carthamine, prepared by means of methyl sulphate. Three grams of the dark coloured powder were shaken with 80 c.c. of 1 per cent. sodium carbonate solution, and 10 c.c. of Merck's perhydrol were then added. After keeping overnight, the yellow liquid was filtered, and the filtrate extracted with ether. On evaporating the ether, an orange coloured, crystalline mass was obtained, which possessed a strong aromatic odour. The product was crystallised from alcohol, employing animal charcoal, and was obtained in pale yellow needles, melting at  $170^{\circ}$ . (Found, C=67.00; H=5.84.  $C_{10}H_{10}O_3$  requires C=67.41; H=5.62 per cent.) This acid was found to consist of *p*-methoxycinnamic acid. The alcoholic mother liquor contained the highly aromatic substance above referred to, and this could be isolated on account of its insolubility in sodium hydrogen carbonate solution. The quantity obtained has as yet been too small for analysis, but it most probably consists of *p*-methoxycinnamaldehyde, a substance which has apparently not yet been synthesised.

*Oxidation with Chromic Acid.* The oxidation of the crude carthamine methyl ether with chromic acid at the ordinary temperature was also carried out. The main product of the reaction, soluble in ether, was a colourless, crystalline acid, which melted at  $180^{\circ}$ , and was found to consist of anisic acid. A small quantity of a second substance, which was insoluble in sodium hydrogen carbonate solution, was also isolated, and this possessed the characteristic odour of anisaldehyde.

According to Schlieper (*loc. cit.*), when carthamine is digested with boiling alcohol, it is slowly converted into a yellow substance of the formula  $C_{14}H_{14}O_6$  and Radcliffe (*loc. cit.*) also states that it was noted that alcoholic solutions of carthamine rapidly decompose with the production of a yellow colouring matter. Attempts to

repeated these experiments were, curiously enough, quite unsuccessful, and no yellow substance was produced from carthamine by digesting its solutions in methyl alcohol, ethyl alcohol, or the ordinary laboratory spirit at the boiling point for long periods, or under pressure at 100° in sealed tubes. It is most likely, therefore, that the production of this yellow substance must have arisen from the action of some impurity present in the carthamines of Schlieper and Radcliffe, or in the alcohol they employed, although experiment showed that as regards the latter this could not have been due to acetone. On the other hand, it has been shown that Radcliffe's substance, both in melting point and solubility, differs markedly also from pure carthamine, and it suggests itself as possible that his compound was a potassium salt of the colouring matter, and that this, as one would anticipate, is less stable than carthamine itself.

That carthamine shows a tendency to give a yellow product was ascertained during some experiments on its acetylation\* in the presence of sulphuric acid. Thus, if the colouring matter is suspended in acetic anhydride to which a few drops of sulphuric acid have been added, and the mixture kept for some days or is heated for a short time on the water bath, an orange-brown substance is precipitated when the product is poured into water. By extracting this compound with benzene, a yellow acetyl derivative is thus dissolved, and this, on hydrolysis with sulphuric acid in the presence of alcohol, yields a bright yellow colouring matter.†

Again, if carthamine is boiled with ammonium carbonate solution, a yellow liquid is obtained, which, when neutralised with acid, does not give a precipitate, and on evaporation to dryness gives an aurine-like mass, very soluble in water.

Aniline under suitable conditions also yields a yellow substance which, however, in this case, is readily crystallised. Two grams of finely powdered carthamine, suspended in 25 c.c. of absolute alcohol were treated with 25 drops of aniline, and the mixture digested at the boiling point for one hour. The carthamine gradually dissolved, and, on cooling, the orange-brown liquid gelatinised. Addition of boiling water caused, however, the formation of a clear solution, from which fine, yellow needles gradually separated, and after keeping overnight these were collected, washed with dilute alcohol with absolute alcohol, and finally with ether. For purification, the substance was dissolved in a little hot pyridine, the solution treated with twice its volume of boiling 50 per cent. alcohol, and the glistening, yellow needles, which separated on

\* When carthamine is acetylated in presence of zinc, a colourless acetyl derivative is obtained, which has yet only been isolated in an amorphous condition.

† An analysis of this compound is withheld until further confirmation is possible.

compound, twice recrystallised in a similar manner. It then melted and decomposed at 276–278°. Finally, some portion of the compound was dissolved in boiling acetic acid by the aid of a few drops of water, the solution diluted with boiling water, and, when cold, the crystals collected and again recrystallised by this process. The latter treatment, however, proved to be unnecessary, for it was ascertained that no alteration in the decomposition point had been thus effected. The substance contained nitrogen, and the yield averaged about 30 per cent. of the carthamine employed. For analysis it was dried at 160°.

Found, C = 61.10, 60.71, 60.92; H = 4.73, 5.05, 5.26; N = 2.65, 2.72.

$C_{27}H_{31}O_{11}N$  requires C = 61.08; H = 5.09; N = 2.29 per cent.

This substance, which, on heating, develops a bright orange tint, and for which the name *aniline ranthocarthamate* is proposed, can also be prepared by boiling carthamine in pyridine solution with a little aniline. During its preparation very little decomposition occurs; that is, in the sense of the formation of products soluble in ether.\* It is almost insoluble in boiling alcohol, slightly more soluble in boiling acetic acid, and dissolves in alkaline solutions with a pale yellow colour. If the alkaline liquid is neutralised with hydrochloric acid in the cold, a gelatinous precipitate separates, which, when collected and washed with water, gradually dissolves, but if the acidified mixture is kept for some time or is gently warmed, the precipitate becomes more granular, is then insoluble in water, and has the decomposition point of the original substance. In a second experiment employing 10 per cent. potassium hydroxide solution, the solution was kept for some time, and the precipitate produced from it by acetic acid, crystallised from dilute alcoholic pyridine and submitted to analysis:

Found, C = 60.77; H = 5.03 per cent.

It decomposed at 273–274°, and was evidently the original compound. By boiling with acetic anhydride, it slowly dissolves, but decomposition gradually occurs, and the solution becomes olive coloured.

For the purpose of obtaining further information as to the molecular weight of this compound, the  $\beta$ -naphthylamine derivative was prepared by boiling a mixture of 2 grams of carthamine, 1.5 grams of  $\beta$ -naphthylamine, and 30 c.c. of alcohol for one hour. The product was treated with boiling water, and the crystals which separated on cooling were collected and allowed to drain on porous

\* The dilute alcoholic mother liquid, when acidified and extracted with ether, gave a trace of a crystalline residue, which contained *p*-coumaric acid and a substance resembling *p*-hydroxybenzaldehyde.

porcelain. When almost dry, the product was made into a thin cream with alcohol, the insoluble residue collected, washed with alcohol, and crystallized three times from dilute alcoholic pyridine. For analysis it was dried at  $160^{\circ}$ :

Found, C=63.47; H=5.09; N=2.18.

$C_{25}H_{25}O_{12} \cdot C_{10}H_9N$  requires C=63.73; H=5.01; N=2.12 per cent.

$\beta$ -Naphthylamine xanthocarthamate forms beautiful orange-coloured leaflets, which, when heated, become bright scarlet coloured, sinter at about  $260^{\circ}$ , and melt and decompose at about  $266$ – $268^{\circ}$ . It dissolves in alkaline solutions with a pure yellow colour, and after some time a precipitate separates, which has the properties of  $\beta$ -naphthylamine.  $\psi$ -Cumidine also reacts with carthamine, giving a product crystallising in glistening, orange coloured leaflets, which sintered at  $285^{\circ}$ , and melted and decomposed at about  $290^{\circ}$ . When dissolved in alkaline solutions, the pale yellow liquid possesses the characteristic odour of  $\psi$ -cumidine, and gradually deposits crystals of this base. Attempts to prepare the *p*-chloroaniline derivative in a pure condition, and made with the object of obtaining a chlorine estimation, gave a gelatinous product, which was not readily crystallised.

As far as the evidence is therefore available, these compounds are probably the salts of an acid provisionally termed *xanthocarthaminic acid*. This compound, which would appear to be isomeric with carthamine, is closely allied to it, and preliminary experiments indicate as probable that it can be reconverted into this colouring matter in a simple manner.\* Owing to lack of material, no serious attempt could be made to isolate the free acid, and such information which has been obtained as to this substance will be given after a fuller confirmation of its properties.

These yellow compounds indicate that the molecular weight of carthamine is high, being apparently represented by the formula  $C_{25}H_{25}O_{12}$ , and it was interesting to obtain further confirmation of this point by the preparation, if possible, of a potassium salt. When an alcoholic solution of carthamine is treated with potassium acetate, a colloidal precipitate of the potassium salt is formed, and to isolate this in a crystalline condition the following method was adopted. Finely powdered carthamine, suspended in boiling alcohol, is treated drop by drop with strong aqueous potassium acetate until a clear solution is produced. On cooling, crystals separate out, and

\* When a cold solution of  $\beta$ -naphthylamine xanthocarthamate is treated with alkali and, after keeping, is repeatedly extracted with ether to remove  $\beta$ -naphthylamine, the alkaline liquid when neutralised with hydrochloric acid gradually deposits a curdy, yellow precipitate. On keeping for some days, this slowly becomes red-coloured, and when dissolved in pyridine gives a red solution, closely resembling in tint that given by carthamine with the same solvent.



These are collected, washed with absolute alcohol, then with ether, and dried at  $160^{\circ}$ .

Found, K = 6.94, 7.28.

$C_{22}H_{24}O_{12}K$  requires K = 7.04 per cent.

This potassium salt consists of green, iridescent needles, and is decomposed with hot water with liberation of the free colouring matter. On this account an excess of water must not be added during its preparation.

In connexion with the molecular weight of carthamine, it was also interesting to determine the water of crystallisation in the pure air-dry material, evidence of the presence of which was shown by the hygroscopic nature of the anhydrous substance. In carrying out these experiments, the colouring matter was freed from pyridine by drying at  $160^{\circ}$ , was kept in air until its weight was constant, and the loss occasioned by heating it to  $160^{\circ}$  again determined:

Found,  $H_2O$  = 6.79, 6.57, 6.70.

$C_{22}H_{24}O_{12} \cdot 2H_2O$  requires  $H_2O$  = 6.52 per cent.

Finally, experiments were carried out by the ebullioscopic method to ascertain the molecular weight of carthamine, employing methyl alcohol and pyridine as solvents, but without success, due in the first case to the limited solubility of the substance, and in the second apparently to slow decomposition at the boiling temperature. Application was therefore made to Dr. Barger, who very kindly consented to experiment on the subject by means of his microscopic method (Trans., 1904, 85, 286), employing pyridine as a solvent. The results in three distinct experiments in which azobenzene was used for comparison were M.W. = 566, 537, and 551, whereas the formula  $C_{22}H_{24}O_{12}$  requires M.W. = 516. These figures, taken in conjunction with the analytical numbers given by the aniline and  $\beta$ -naphthylamine xanthocarthaminates, the determinations of water of crystallisation, and the somewhat less trustworthy evidence given by the potassium salt, indicate that the formula of carthamine is, or closely approximates to  $C_{22}H_{24}O_{12}$ . The fact that carthamine, when hydrolysed with alkali, has given only *p*-coumaric acid and *p*-hydroxybenzaldehyde is peculiar in view of the fact that this compound contains so much oxygen, and that its benzoyl derivative indicates the presence of six or seven hydroxyl groups. In view of the numerous experiments which have been made on this point, it is hardly likely that a phenol is also produced during this decomposition. Although a final experiment, employing some quantity of the dye, will, it is hoped, be carried out at a later date. The recent work of Dimroth on carminic acid (Ber., 1909, 32, 1611) and of the same author on carthamine acid (ibid., 1910, 33, 1387) indicates that in addition to a

saphranine group, these dyestuffs contain a second nucleus, which is probably of an aliphatic nature, and it seems possible that in carthamine a group or groups of this character may exist.

It is unfortunate that at present no crystalline derivatives of carthamine have been prepared, but it is to be remembered, in regard to the very important colouring matter of logwood, hematein, the constitution of which is now clear, that such is also the case. The fact that carthamine so readily yields a yellow compound suggests that the yellow colouring matter of safflower may be connected with this reaction. This compound, which up to the present has only been isolated in the form of a syrup readily soluble in water, appears to contain a glucoside, and by digestion with boiling dilute sulphuric acid a small quantity of a crystalline, yellow substance has been isolated from it by means of ether. A further study of this product will be carried out as soon as the necessary raw material is available, and the continuation of this work on carthamine will shortly be resumed.

The authors are indebted to the Research Fund Committee of the Chemical Society for a grant, which has been partly employed to cover the heavy expense of this investigation.

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### CXXXI.— $\Delta^1$ -*p*-Menthenol(8) and $\Delta^1$ -*p*-Menthadiene.

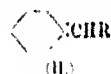
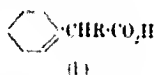
By WILLIAM HENRY PERKIN, jun., and OTTO WALLACH.

THE difficulty of preparing substances belonging to the terpene group in a state of purity becomes more and more apparent as the chemistry of this group gradually develops, and this difficulty is most marked in the case of the terpenes themselves.

It is true that the presence even of considerable quantities of impurity does not always interfere with the characterisation of the substance in question. Thus, for example,  $\alpha$ -terpinene ( $\Delta^1$ -*p*-dihydrocymene or  $\Delta^1$ -*p*-menthadiene) can be readily detected in mixtures by means of its nitrosite or by oxidation to  $\alpha$ -dihydroxy- $\alpha$ -methyl- $\beta$ -isopropyladipic acid, although it has, so far, not been found possible to isolate the hydrocarbon in a pure state. It is also a comparatively simple matter to demonstrate the formation of dipentene during a reaction, although no method is known by

which synthetical dipentene can be obtained quite free from isomerides or oxy-derivatives, such as cineol. On the other hand, small quantities of impurity interfere in a very serious way with the accurate measurement of physical properties, and it is, for this reason, often very difficult to determine with certainty the effect of slight changes in constitution on the physical properties of the terpenes. As an example of this, mention may be made of the widely differing values given by various investigators for the molecular refraction of a terpinene, and of the difficulty which has been experienced of accurately determining the boiling point of dipentene. The preparation, in a pure condition, of alcohols and ketones of the terpene group does not usually present the difficulties which have so frequently been observed in the case of the terpenes themselves, because it is often possible to convert such alcohols or ketones into well-crystallised derivatives from which the parent substance may be regenerated, and the accurate determination of the physical constants of such alcohols or ketones is therefore a comparatively simple matter. In order to obtain a terpene in a pure state, it is best to prepare it synthetically, but, even in the case of syntheses which appear to proceed in a simple manner, there is always risk of intramolecular change, and recent investigations have emphasized the remarkable tendency exhibited by certain groupings in this respect.

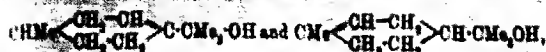
In illustration of this, it is only necessary to call attention to the conversion of substances of the type (I) into hydrocarbons of the type (II), a change which has often been observed to take place



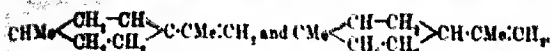
during the elimination of carbon dioxide at comparatively low temperatures.

In order to be quite certain of the constitution of a given terpene, it is usually necessary to prepare it in several different ways, and it was with this object in view that we decided jointly to investigate certain terpenes and their derivatives, the accurate determination of the physical properties of which is of importance in connexion with the question of the effect exerted by double linkings in different positions. The present communication deals with 1<sup>st</sup> *p*-mentheol(8) and 1<sup>st</sup> *p*-menthadione, substances which had already been prepared by W. H. Perkin, jun., and S. S. Pickles (Trans. 1905, 87, 639), and contains a description of an entirely new method for the preparation of these substances discovered by O. Wallach.

$\Delta^3$ -menthenol(8) differs from  $\alpha$ -terpineol,



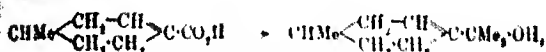
in the position of the double linking, and  $\Delta^3$ - $\alpha$ -menthadieNE differs from limonene,



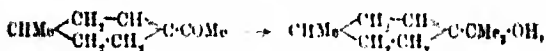
not only in this respect, but also in the relation of the double linkings to one another.

In the case of  $\Delta^3$ - $\alpha$ -menthadieNE, the two ethenoid linkings are conjugated, a condition of things which causes the molecular refraction of this substance to exhibit exaltation above that of limonene (compare Trans, 1906, 89, 855).

Two methods are now available for the preparation of  $\Delta^3$ -menthenol(8). Perkin and Pickles (*loc. cit.*) obtained this alcohol from the ester of  $\Delta^3$ tetrahydro p-toluic acid (1-methyl- $\beta$ -cyclohexene-4-carboxylic acid) by the action of the Grignard reagent:



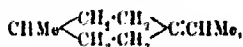
whereas Wallach (*Annalen*, 1909, 365, 272) synthesised 4-acetyl-1-methyl- $\Delta^3$ cyclohexene, and then converted this substance into  $\Delta^3$ -menthenol(8):



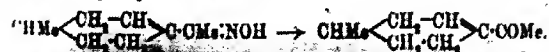
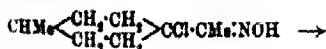
and an account of this method is given in the present communication.

#### 4-Acetyl 1-methyl- $\Delta^3$ cyclohexene.

In preparing this ketone, the semicyclic hydrocarbon, 1-methyl-4-ethylidenecyclohexane,



is converted into the nitrosochloride, and this, by elimination of hydrogen chloride, into the oxime, from which the ketone is obtained by hydrolysis:

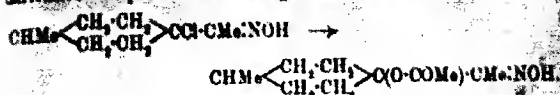


The fact that 1-methyl-4-ethylidenecyclohexane may now be prepared in considerable quantities has made the investigation of several interesting stereo-isomeric derivatives possible. The nitroso-chloride, which is obtained in an excellent yield by the process already described, may be separated, by repeated crystallisation from acetone,\* into two distinct substances. The more sparingly soluble component crystallises in needles, and melts at 117–118°, the more readily soluble isomeride crystallises in plates and melts at 113–114°; both are volatile in steam. The higher melting substance yields, on careful treatment with piperidine a nitropiperidide melting at 130–131°, and the same treatment converts the isomeride into a nitropiperidide which melts at 119–120°. Both crystallise from methyl alcohol in such similar forms that it is almost impossible to distinguish them by their appearance only. During the determination of the melting point of the nitropiperidide melting at 119–120°, the observation was made that the substance, after it had crystallised in the tube, melted at a higher temperature than before. When larger quantities were melted in a test-tube, a strong odour of piperidine was noticed, showing that partial decomposition into the oxime was taking place (compare Wallach, *Terpene und Campher*, p. 80).

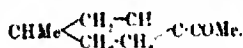
The residue, after crystallisation, melted at 130–131°, showing that a conversion of the lower melting nitropiperidide into the isomeride of higher melting point had taken place. That these nitropiperidides are merely stereo-isomeric and not chemically distinct is proved by the fact that both, on elimination of hydrogen chloride, yield the same oxime. In preparing the oxime of 4-acetyl-1-methyl- $\Delta^1$ -cyclohexene, the crude nitroso-chloride may therefore be employed, and experience has shown that it is better to avoid the use of sodium methoxide for the elimination of the hydrogen chloride. In some cases this reagent has been found to be useful, but as a rule it is to be avoided because of the possibility of the formation of methoxy-derivatives from the nitroso-chloride by the exchange of chlorine for methoxyl (compare Deussen, *Annalen*, 1909, 369, 62). Traces of such methoxy-derivatives are difficult to remove, and are apt to give rise to inaccurate observations of the properties of the oximes (compare *Annalen*, 1908, 359, 303). In the present instance, the sodium acetate and acetic acid method was employed for the elimination of the hydrogen chloride with excellent results (Wallach, *Terpene und Campher*, p. 86), and during the investigation of the products, the observation was made

\* For observations on the suitability of acetone for the crystallisation of nitroso-chlorides and similar derivatives, compare Wallach, *Terpene und Campher*, p. 65, and *Annalen*, 1904, 336, 43.

for the first time that a relatively stable intermediate acetyl derivative was produced according to the scheme:



The acetate, which in this case is crystalline, is decomposed on distillation into acetic acid and the unsaturated oxime.



In preparing the oxime, it is best to distil the product of action of sodium acetate on the nitroso chloride, first under diminished and then under the ordinary pressure, the product is then crystallised from methyl alcohol, when the oxime (m. p. 116–117°) is readily obtained pure.

If the acetate, which when quite pure crystallises in large, transparent crystals and melts at 111–112°, is not completely decomposed before the crystallisation of the oxime, crops of crystals separate from the mother liquor, which melt at about 85° and consist of a mixture of the oxime and the acetate. This mixture is much more soluble in methyl alcohol than the components, and can only be separated into these by tedious fractional crystallisation.

In preparing 4-acetyl-1-methyl  $\Delta^1$ -cyclohexene, the pure oxime is decomposed by warming with dilute sulphuric acid, and subsequent distillation in a current of steam. The resulting ketone always contains traces of oxime which have escaped hydrolysis, and in this, as in all other similar cases, if the pure ketone is required, it is necessary to purify the crude product by converting it into the semicarbazone.

This derivative (m. p. 222°) is then decomposed by dilute sulphuric or oxalic acid, and the ketone purified by distillation under ordinary pressure. The properties of 4-acetyl-1-methyl  $\Delta^1$ -cyclohexene are the following:

B. p. 210–211°,  $d_4^{20}$  0.942,  $n_D^{20}$  1.4830 at 20°.

M 41.22. Calculated for  $\text{C}_9\text{H}_{16}\text{O}$ , M 41.84.

0.1703 gave 0.4887  $\text{CO}_2$  and 0.1581  $\text{H}_2\text{O}$ . C = 78.3; H = 10.4.

$\text{C}_9\text{H}_{16}\text{O}$  requires C = 78.2; H = 10.2 per cent.

At low temperatures the ketone solidifies to a crystalline mass, which melts again at about -20°; it is rather soluble in water, and has an odour resembling aniseed. 4-Acetyl-1-methyl  $\Delta^1$ -cyclohexene is isomeric with 4-acetyl-1-methyl  $\Delta^2$ -cyclohexene, which is obtained by the oxidation of  $\beta$ -terpineol (m. p. 32°), the isomerism being due merely to the position of the ethenoid linking. The

following table gives an interesting comparison of the properties of the two isomerides:

	4-Acetyl-1-methyl- $\Delta^3$ -cyclohexene.	1-Acetyl-1-methyl- $\Delta^3$ -cyclohexene.
B. p.	205—206°	210—211°
d	0.940	0.942
n <sub>D</sub> <sup>20</sup>	1.4719	1.4830
M	41.10	41.24
M. p. of osime	51°	116—117°
M. p. of semicarbazone	165°	227°

The differences in the physical properties of the two ketones are in agreement with the generalisation which K. Auwers and F. von der Heyden (*Ber.*, 1909, 42, 2406) and others have deduced as the result of the examination of a large number of cases, and which is briefly as follows. Experience shows that, when a double linking in a position removed from the carbonyl group becomes conjugated with that group, there is an increase in the boiling point, density and refractive index, and of these properties the increase in the refractive index is the most evident in the particular case under review.

*Conversion of 4-Acetyl-1-methyl- $\Delta^3$ -cyclohexene into  $\Delta^3$ p-Menthenol(8).*

The conversion of the ketone into the tertiary alcohol was carried out under the following conditions. The ketone (20 grams) dissolved in dry ether (60 c.c.) was gradually added to a Grignar solution prepared from magnesium (6 grams), methyl iodide (3 grams), and ether (110 grams), and the whole heated for two hours on the water-bath. The product was decomposed with water, and distilled in a current of steam, the receiver being changed as soon as the ether had passed over. It was frequently noticed that  $\Delta^3$ menthenol crystallised in the condenser and receiver, but traces of impurity are sufficient to prevent crystallisation, and, unless crystal is introduced, the pure substance will sometimes remain in weeks without crystallising (compare p. 1435):

0.1560 gave 0.4462  $\text{CO}_2$  and 0.1632  $\text{H}_2\text{O}$ . C = 78.0; H = 11.7.

$\text{C}_{10}\text{H}_{18}\text{O}$  requires C = 77.8; H = 11.7 per cent.

$\Delta^3$ p-Menthenol(8) melts at 39—40°, and distils at 97°/14 mm or at 205° under the ordinary pressure. It has a strong and very pleasant odour, resembling that of  $\alpha$ -terpineol, and, in contact with acids, it very readily loses water with formation of  $\Delta^3$ menthadiene.

It exhibits in a marked degree the property of superfusion.

fact which much facilitates the determination of its physical constants. The following values were observed:

$$d_4^{20} = 0.921, n_D^{20} = 1.4769 \text{ at } 18^\circ.$$

$$M = 47.16. \text{ Calculated for } C_{10}H_{17}OH \quad M = 47.19.$$

$\Delta^1$ -p-Menthenol(8) does not yield a crystalline derivative on treatment with nitrosyl chloride, but it combines with phenylcarbimide, and the phenylurethane,  $C_{10}H_{17}O \cdot CO \cdot NH \cdot C_6H_5$ , after crystallization from methyl alcohol, melts and decomposes at about  $128^\circ$ . The melting point varies, however, considerably according to the rapidity with which the substance is heated, and a rapid determination gives a melting point some degrees higher than  $128^\circ$ .

*Preparation of  $\Delta^1$ -p-Menthenol(8) and  $\Delta^1$ - $\alpha$ -p-Menthadiene from p-Toluenic Acid.*

This synthesis was first carried out by Perkin and Pickles in 1905 (Trans. 87, 639). The first step consists in the reduction of p-toluenic acid to 1-methylcyclohexane-4-carboxylic acid (hexahydro-p-toluenic acid) by treatment in boiling isamyl alcoholic solution with a large excess of sodium. Since this process is very laborious and unpleasant, a series of experiments was made with the object of determining whether the reduction might not be effected in ethyl-alcoholic solution, but without result. Even when alcohol which had been twice distilled over calcium was employed (compare Trans., 1909, 95, 1876, footnote), and the process carried out as vigorously as possible, no appreciable reduction took place. The whole of the material required for this investigation had, therefore, to be prepared by the original method (*loc. cit.*, p. 643), but certain modifications were introduced with advantage. The crude hexahydro-acid, obtained on acidifying the product of reduction, was distilled in a current of steam, and thus separated from resinous matter, when, in most cases, it was found that the colourless acid collected from the distillate, after crystallising from dilute acetic acid, melted at  $112^\circ$ , and was quite pure. If this was not the case, it was treated in alkaline solution with a little permanganate in the usual manner. The bromination of the pure 1-methylcyclohexane-4-carboxylic acid was carried out exactly as previously described (*loc. cit.*, p. 645), and the product poured into excess of alcohol and thus converted into ethyl 1-bromomethylcyclohexane-4-carboxylate (ethyl  $\alpha$ -bromohexahydro-p-toluate). In the original experiments the elimination of hydrogen bromide from this ester was brought about by boiling alcoholic potassium hydroxide, but it is better to digest the crude ester with four times its volume of diethylaniline for two hours in a reflux apparatus.



extracted with ether, the ethereal solution washed with dilute hydrochloric acid, dried, evaporated, and the ester distilled under diminished pressure, when almost the whole quantity distils at 148–152°/100 mm., the yield being nearly quantitative. The ethyl 1-methyl- $\Delta^1$ -cyclohexene-4-carboxylate (ethyl  $\Delta^1$ -tetrahydro-*p*-toluate) thus obtained was hydrolysed by methyl-alcoholic potassium hydroxide and the acid twice crystallised from dilute acetic acid, when it melted at 134°, and was quite pure. This acid (40 grams) was next digested with alcohol (250 c.c.) and sulphuric acid (20 c.c.) for two hours, and the ester, after isolating in the usual manner, distilled at 152–153°/100 mm. (Found, C=71.4; H=9.6. Calc., C=71.4, H=9.5 per cent.)

On the former occasion (*loc. cit.*, p. 647) it was observed that this ester, when treated with magnesium methyl iodide, did not behave normally, since it was largely converted directly into  $\Delta^1$ -*p*-menthadiene, the yield of  $\Delta^1$ -*p*-menthenol(8) being very small.

In order, if possible, to avoid this dehydration, the ester (20 grams), diluted with five times its volume of ether, was cooled in ice and salt, and the ethereal solution of the magnesium methyl iodide (containing 8 grams of magnesium) gradually added. After being kept in the freezing mixture for four hours, the product was left overnight at the ordinary temperature, and then decomposed with water and dilute hydrochloric acid in the usual manner. The resulting oil was mixed with methyl-alcoholic potassium hydroxide (KOH=5 grams), and allowed to remain for twenty-four hours in order to remove any trace of unchanged ethyl 1-methyl- $\Delta^1$ -cyclohexene-4-carboxylate. Water was then added, the neutral oil extracted with ether and distilled in a current of steam, the distillate was again extracted with ether, the ethereal solution dried carefully, and fractionated under diminished pressure, when about three-fourths distilled at 90–95°/30 mm., and consisted almost entirely of  $\Delta^1$ -*p*-menthadiene, elimination of water having taken place in spite of the precautions which had been observed. The remainder, on repeated fractionation, yielded a pure specimen of  $\Delta^1$ -*p*-menthenol(8), which distilled at 108–110°/30 mm., and crystallised at once when a crystal of the pure menthenol was introduced into the well-cooled oil. The mass was left in contact with porous porcelain until quite free from traces of oily impurity and then analysed. (Found, C=77.8; H=11.8. Calc., C=77.9; H=11.7 per cent.)

$\Delta^1$ -*p*-Menthenol(8) melts at 40–41°, and exhibits in a remarkable manner the phenomenon of superfusion (compare *Trans.*, 1906, 89,

801). Some of the pure substance was melted in a small sealed tube and left in the ice chest for three weeks, and, although it was repeatedly shaken, it could not be made to crystallise.

The tube was sent by post from Manchester to Göttingen in the winter time, and the substance arrived still fluid, but when a crystal was introduced the whole solidified at once to a hard, crystalline mass.

The phenylurethane, prepared in the usual manner, separated from dilute methyl alcohol in colourless needles, and melted, when rapidly heated, at  $133-134^\circ$  with decomposition. If, however, the determination was carried out slowly, the observed melting point was a few degrees lower:

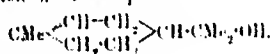
0.1411 gave 6.1 c.c.  $N_2$  at  $15^\circ$  and 758 mm.  $N = 5.2$ .

$C_{17}H_{22}O_2N$  requires  $N = 5.1$  per cent.

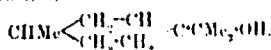
This preparation was mixed with an equal quantity of a specimen of the phenylurethane which had been prepared from  $\Delta^3$ -p-menthenol(8) from 4-acetyl-1-methyl  $\Delta^3$ -cyclohexene (p. 1432), and the mixture melted at the same temperature as the components.

In connexion with the study of the influence of the position of the ethenoid linking on physical properties, it is very interesting to make a comparison of the physical properties of the known pmenthenols, namely:

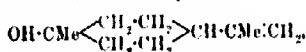
I.  $\Delta^3$ -p-Menthenol(8), or  $\alpha$ -terpinol.



II.  $\Delta^3$ -p-Menthenol(8),



III.  $\Delta^{10}$ -p-Menthenol(1), or  $\beta$ -terpinol.



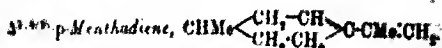
and we therefore append the following table:

	I.	II.	III.
Boiling point.....	$218^\circ$	$205^\circ$	$209-210^\circ$
Melting ".....	$35^\circ$	$39^\circ$	$32^\circ$
$d_4^{20}$ .....	0.938	0.921	0.919
$n_D^{20}$ .....	1.4820	1.4764	1.4740
Melting point of the phenylurethane.....	$113^\circ$	$125^\circ$	$85^\circ$

The examination of these values discloses a remarkable relationship, since it is evident in this case that the approach of the ethenoid linking to the oxygen group causes a fall in boiling point, density, and refractive index, whereas the melting point rises.

In the case of the two ketones compared on p. 1432, exactly the

reverse was shown to be the case. Further experiments are necessary in order to show whether this relationship holds good in other series, and whether it will be possible to draw valid conclusions as to constitution from comparisons such as these.



It has already been mentioned that  $\Delta^1$ - $p$ -menthenol(8) loses the elements of water with great ease, and not only is this the case when it is treated with dehydrating agents, such as potassium hydrogen sulphate, but also when it is left in contact with dilute acids under conditions which, in the case of terpineol, bring about addition of water and formation of terpin. Thus, when the substance is shaken mechanically with 1 per cent. sulphuric acid for several days or warmed at  $80^\circ$  with 5 per cent. aqueous oxalic acid, it loses water with the formation of  $\Delta^{1,8(9)}$ - $p$ -menthadiene. A specimen of the hydrocarbon, prepared by the latter process, was purified, by distillation in a current of steam and subsequent repeated fractionation over sodium, and analysed:

0.1202 gave 0.3882  $\text{CO}_2$  and 0.1314  $\text{H}_2\text{O}$ .  $\text{C} = 88.1$ ;  $\text{H} = 12.2$ .

$\text{C}_{10}\text{H}_{16}$  requires  $\text{C} = 88.1$ ;  $\text{H} = 11.9$  per cent.

$\Delta^{1,8(9)}$ - $p$ -Menthadiene has an odour which can scarcely be distinguished from that of limonene, and the determination of its physical properties gave the following values:

B. p.  $184^\circ$ – $185^\circ$ ,  $d_{15} = 0.858$ ,  $n_D = 1.4924$  at  $19^\circ$ .

$M = 46.02$ . Calculated for  $\text{C}_{10}\text{H}_{16}$   $M = 45.24$ .

It does not yield crystalline derivatives on treatment with halogen acids, nitrosyl chloride, or oxides of nitrogen (compare Perkin and Pickles, *Trans.*, 1906, 89, 618). The constitution of the terpene was controlled by oxidation with 1 per cent. permanganate at  $0^\circ$ , when a solid acid was obtained which, after crystallisation from a mixture of benzene and light petroleum, melted at  $94^\circ$ – $96^\circ$ . The silver salt was analysed. (Found,  $\text{Ag} = 57.5$ .  $\text{C}_7\text{H}_{10}\text{O}_4\text{Ag}$  requires  $\text{Ag} = 57.8$  per cent.)

There can be no doubt that this acid was  $\beta$ -methyladipic acid, and its formation is in harmony with the position of the double linking in  $\Delta^{1,8(9)}$ - $p$ -menthadiene, since, if the double linking were in any other position, or if both double linkings were in the ring,  $\beta$ -methyladipic acid could not have been produced on oxidation.

The examination of the physical constants given above shows at once that the terpene produced by the dehydration of  $\Delta^1$ - $p$ -menthenol(8) by treatment with 5 per cent. aqueous oxalic acid exhibits a remarkably high boiling point, density, and refractive index, and

these high constants are readily explained by the assumption that the molecule contains conjugated ethenoid linkings.

Key and Perkin (Trans., 1906, 89, 849) had previously prepared  $\Delta^1$ - $\Delta^2$ - $\beta$ -menthadiene from  $d$ - $\Delta^1$ - $\beta$ -menthenol(8) by warming with magnesium methyl iodide, and this active terpene exhibited the same properties as the inactive specimen just mentioned, namely, b. p.  $184^{\circ}/748$  mm.,  $d_{20} = 0.8574$ , and  $M = 146.0$ . On the other hand, the inactive  $\beta$ -menthadiene prepared by Perkin and Pickles (Trans., 1905, 87, 639), while boiling at the same temperature, had the low density,  $d_{20} = 0.8358$ . The amount of inactive terpene available at that time was very small, and there is therefore every reason to suppose that the low density was due to the presence of small quantities of impurity. Since, however, the accurate determination of the physical constants in this case is of particular importance, the synthesis of the hydrocarbon by the laborious method employed by Perkin and Pickles (*loc. cit.*) was undertaken on a much larger scale than before, and resulted in the preparation of no less than 50 grams of inactive  $\Delta^1$ - $\Delta^2$ - $\beta$ -menthadiene. This hydrocarbon, after purification by distillation in a current of steam and repeated fractionation over sodium, yielded the following analysis and physical constants:

0.1913 gave 0.6169  $\text{CO}_2$  and 0.2038  $\text{H}_2\text{O}$ .  $C = 87.9$ ;  $H = 11.8$ .

$\text{C}_{10}\text{H}_{16}$  requires  $C = 88.1$ ;  $H = 11.9$  per cent.

B. p.  $184-188^{\circ}$ ,  $d_{20} = 0.8600$ ,  $n_D^{20} = 1.4915$  at  $20^{\circ}$ ,  $M = 145.84$ .

The comparison of the physical properties of the two specimens of  $\Delta^1$ - $\Delta^2$ - $\beta$ -menthadiene prepared (I) from 4 acetyl-1-methyl- $\Delta^1$ -cyclohexene and (II) from 1-methyl  $\Delta^1$ -cyclohexene-4-carboxylic acid exhibits such a close agreement that there can be little doubt that this terpene is now correctly characterized.

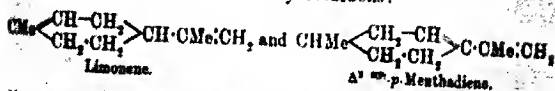
	B. p.	$d_{20}$	$n_D^{20}$	M.
I.	$184-185^{\circ}$	0.858	1.4924	146.02
II.	$184-186^{\circ}$	0.860	1.4915	145.84

Calculated for  $\text{C}_{10}\text{H}_{16}$ ,  $n_D^{20} = 1.4524$

Limonene, on the other hand, has

	B. p.	$d_{20}$	$n_D^{20}$	M.
	$175-176^{\circ}$	0.845	1.4746	152.28

When the formulae of the two hydrocarbons:



are compared, it is evident that the approach of the ethenoid linkings to the conjugated position has resulted in a very considerable rise in boiling point, density, and refractive index, and

this change in the constants is of the same order as that shown by the ketones (p. 1432), but the reverse of that exhibited by the alcohols (p. 1435).

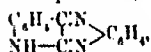
The facts which we have established in this research seem to suggest an explanation for the observation which has so often been made that, in the synthetical preparation of dipentene, substances are always produced which boil higher than that hydrocarbon, and yet are not terpenolene. It is possible that the reagents employed may cause partial intramolecular change to take place, and that the ethenoid linking in the ring may wander from the  $\Delta^1$  to the  $\Delta^3$  position. This point might be decided by the investigation of the amount of bromine absorbed by the higher fractions obtained during the preparation of dipentene, since Perkin and Pickles (Trans., 1905, 87, 641) have shown that  $\Delta^{3,6,9}$ -*p*-menthadiene, owing to its containing conjugated ethenoid linkings, is only capable of absorbing two atoms of bromine, whereas dipentene, under the same conditions, yields dipentene tetrabromide.

MANNHEIM AND GÖTTINGEN

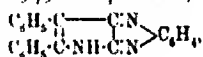
## CXXXII. *Cyclic Di- and Tri-ketones.*

By SIEGFRIED RUEHMANN.

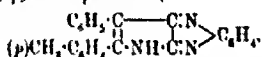
THE close resemblance between isatin and the diketopyrrolines, which has been pointed out previously (Trans., 1909, 95, 934, 1603; 1910, 97, 462), exists also in the behaviour of these substances towards *o*-phenylenediamine. In the same way as this diamine condenses with isatin to indophenazine,



it yields similar compounds with the diketopyrrolines. I have prepared, thus, *diphenylpyrrolinophenazine*,



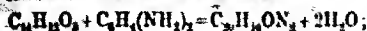
and *phenyl p-tolylpyrrolinophenazine*,



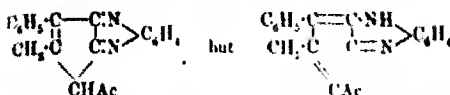
which substances, like indophenazine, are yellow.

The red diketocyclopentene derivative,  $\text{C}_{14}\text{H}_{12}\text{O}_2$ , which is formed from the product of the action of sodioacetylacetone on phenyl

phenyl chloride (Rubemann and Merriman, *Trans.*, 1905, 87, 1383) also condenses with the diamine thus:



but the compound which is produced differs in colour from the phenazines, since it is purple. This fact leads to the conclusion that it has not the constitution:

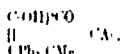


and that its formation is preceded by the change of diketoaethyl-phenylmethylcyclopentene into its tautomeric form:

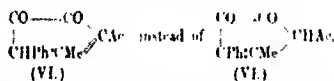


This view as to the formula of the purple condensation product, which is indicated by the similarity of its colour with that of the salts of the diketocyclopentene derivative,  $C_{14}H_{12}O_3$ , is supported by the following considerations. The hydrogen, marked by an

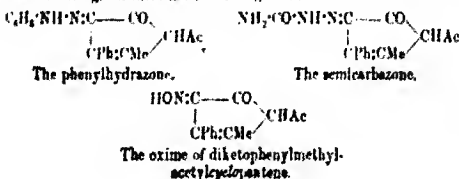
An error occurs in my paper, "Condensation of Amides with Esters of Acetylenic Acids" (*Trans.*, 1909, 95, 284), which requires correction. Whereas the tautomeric form of the cyclopentene derivative,  $C_{14}H_{12}O_3$ , is correctly represented thus:



the formula of the compound with the diketonic grouping (p. 286) is erroneously given as:



After having established the nature of the tautomeric change of this substance by a comparison of its properties with isatin and the diketopyrrolines (*loc. cit.*), another correction becomes imperative. This concerns the formulae of some of the derivatives of the diketone,  $C_{14}H_{12}O_3$ , which were described previously (*Trans.*, 1906, 89, etc.). The formulae given there must be changed to:

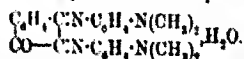


isatin, has a greater mobility than the imino hydrogen of isatin or the diketopyrrolines. Whereas the latter substances, with alkalis, yield blue solutions which quickly change to yellow, the diketocyclopentene derivative,  $C_{14}H_{12}O_2$ , dissolves not only in alkalis, but also in alkali carbonates or acetates, to form blue salts, and these are considerably more stable than the salts of the former diketone. Again, the diketopyrrolines do not give blue solutions on the addition of piperidine, but form with it colourless additive products (this vol., p. 465); the diketocyclopentene derivative,  $C_{14}H_{12}O_2$ , on the other hand, dissolves in piperidine, as it does in alkalis or alkali carbonates, to yield a blue solution. It follows therefore that this diketone readily undergoes a transformation into its tautomeric form, which occurs, also, in its condensation with *o*-phenylenediamine. Reagents, like phenylhydrazine or hydroxylamine, do not effect this change, but form with the diketone a phenylhydrazone or an oxime (Ruhemann, *Trans.*, 1906, 89, 682). Nor does such a transformation occur in the reaction of phenylmercaptan with the diketone, which yields an additive product; this, in every respect, resembles the one which is formed by the union of the mercaptan with diketodiphenylpyrrolone (*loc. cit.*).

On the one hand, the similarity, on the other the difference, which exists between the diketocyclopentene derivative,  $C_{14}H_{12}O_2$ , and isatin, or the diketopyrrolines, induced me to attempt the preparation of diketopentenes with the grouping  $\begin{array}{c} \text{C} \text{---} \text{CO} \\ | \quad | \\ \text{C-CH}_2 \text{---} \text{C} \end{array}$  in which the methylene radicle is intact. With this object in view, as well as for the purpose of arriving at a compound which in constitution closely resembles isatin, I chose  $\alpha$ -hydrindone as starting point. I expected that this substance, by means of Sachs and Barschall's method of changing methylene groups into ketonic groups (*Ber.*, 1901, 34, 2047), would be transformed into 1:2-diketohydrindene.



the isomeride of the known 1:3-diketohydrindene. The experiment, however, led to the remarkable result that, in the presence of potassium hydroxide or sodium carbonate, *p*-nitrodimethylaniline mainly attacks both methylene groups of  $\alpha$ -hydrindone. Analysis of the substance which is formed points to the formula  $C_{20}H_{19}ON_2 \cdot H_2O$ , accordingly, it is to be represented thus:

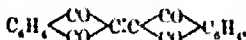


That, indeed, nitrodimethylaniline has entered into both methylene groups of the hydrindone follows from the behaviour of

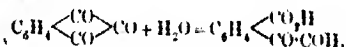
mineral acids towards the condensation product; thus, it is readily decomposed, and yields the hydrate of triketohydrindene.



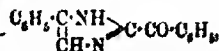
Some years ago Kaufmann (*Ber.*, 1897, 30, 387) stated that he obtained triketohydrindene, along with diphtalylethylene (indene),



an oxidation of 1:3 diketohydrindene by means of hydrogen peroxide, but that the amount which was formed did not suffice for analysis. He described his compound as crystallising from glacial acetic acid in yellowish-brown plates, which were insoluble in alkalis, and decomposed at 190–206°. The substance which is produced from a hydrindone has quite different properties, and fully characterise it as triketohydrindene. It crystallises from water or alcohol in the form of its colourless hydrate, which, on heating, first loses water and turns red, then melts, and decomposes at 239–240°. The triketone readily reduces Fehling's solution and ammoniacal silver solutions. This fact is undoubtedly due to the opening up of the five carbon ring and the formation of the semialdehyde of phthalonic acid, namely, phenylglyoxal- $\alpha$ -carboxylic acid, thus:

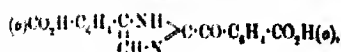


which is finally oxidised to phthalonic acid. Of especial interest is the action of ammonia on the triketone. If the aqueous solution of the mixture of both substances is kept for a short time, it turns a deep reddish-violet, and no longer reduces silver nitrate. On the addition of dilute hydrochloric acid, a red solid is precipitated, which has the empirical formula  $\text{C}_6\text{H}_5\text{O}_2\text{N}$ . This formula, undoubtedly, should be doubled. The constitution of the substance may be deduced from a consideration of the action of ammonia on phenylglyoxal,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{COH}$ . Müller and v. Pechmann (*Ber.*, 1889, 22, 2557), who studied this reaction, did not arrive at the correct empirical formula of the compound which is formed. This was established by Pinner (*Ber.*, 1902, 35, 4134), who showed, also, that the substance was identical with the one which Engler and Haackkamp (*Ber.*, 1885, 18, 2241) obtained on treatment of dibromoacetophenone with ammonia. Pinner, further, considered that it is to be represented thus:

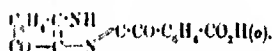




and accordingly to be regarded as 2-benzoyl-5-phenylglyoxaline. Since the reducing action of triketohydrindene can only be explained by the opening up of the five-carbon ring and the formation of phenylglyoxal- $\alpha$ -carboxylic acid, the action of ammonia may be explained, as in the case of phenylglyoxal, by the assumption that the aldehydazul, first, condenses to the dicarboxylic acid,

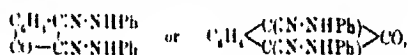


which subsequently loses water and yields:

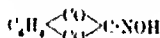


The product thus appears both to contain the indone ring and to be a derivative of glyoxaline. It may therefore be called 2-oxobenzoylindonodiphenylazulone. Experiments to prove the correctness of this view are in progress.

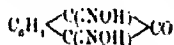
Triketohydrindene condenses with phenylhydrazine to an orange-coloured diphenylhydrazone, the constitution of which is either



I am inclined to regard the first formula as correct; a similar formula would represent the yellow disemicarbazone,  $C_6H_4O(C \cdot N \cdot NH \cdot CO \cdot NH)_2$ , which triketohydrindene forms with semicarbazide. The formation of a trihydrazone or trisemicarbazone does not take place; hydroxylamine, however, is capable of producing a trioxime. Oximes of triketohydrindene are already known, namely, 2-oximino-1-3-diketohydrindene,

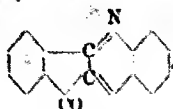


(Wislicenus, *Annalen*, 1888, **246**, 317); further, 1:3-dioximino-2-hydrindone,



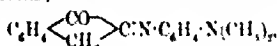
(Heuser and Schieffer, *Ber.*, 1899, **32**, 32), and finally trioximino-hydrindene,  $C_6H_4(C \cdot NOH)_3$ , which Wislicenus and Kostale (*Annalen*, 1889, **252**, 74) prepared by treating 2-oximino-1:3-diketohydrindene with hydroxylamine. The latter substance is the chief product contained in the mixture of oximes which is formed by the action of hydroxylamine on triketohydrindene. Although I have been unable to isolate the trioxime in the pure state, its formation is sufficiently established by the analytical result of the

mixture. Triketohydrindone condenses with *o*-phenylenediamine to ketohydrindonephenazine,



which is yellow.

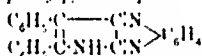
The behaviour of *p*-nitrosodimethylamine towards  $\alpha$ -hydrindone induced me to ascertain whether, besides the compound  $C_{22}H_{20}O_2N_4$ , the dimethylaminoanil,



is formed in the reaction. On examining the mother liquor from the black solid,  $C_{22}H_{20}O_2N_4$ , which separates if the alcoholic solution of the mixture of *p*-nitrosodimethylamine and  $\alpha$ -hydrindone is treated with potassium hydroxide, I found that, in the course of a few days, it deposited a red solid, which separated from alcohol in beautiful red crystals, but the yield was so small that it sufficed only for an analysis. Although the analytical data are not in full agreement with the theory, they indicate that the substance is indeed the dimethylaminoanil of  $\alpha$ -hydrindone.

#### EXPERIMENTAL.

##### *Diphenylpyrrolinophenazine.*



This compound separates as a yellow solid when the mixture of diketodiphenylpyrrolone and *o*-phenylenediamine, dissolved in dilute acetic acid, is digested on the water bath. It is sparingly soluble in cold, moderately so in boiling, alcohol, and crystallises in yellow needles, which melt at  $240-241^\circ$ .

0.1750 gave 0.5272  $CO_2$  and 0.0765  $H_2O$ .  $C = 82.16$ ;  $H = 4.86$ .

0.1355 .. 20.8 c.c.  $N_2$  at  $15^\circ$  and 759 mm.  $N = 13.11$ .

$C_{22}H_{18}N_4$  requires  $C = 82.24$ ;  $H = 4.67$ ;  $N = 13.08$  per cent.

The substance dissolves in cold concentrated sulphuric acid, yielding a solution which is purple in transmitted, green in reflected, light; the solution in hydrochloric acid is red.

*Phenyl-p-tolylpyrrolisphenazine*

This is prepared from diketophenyl-p-tolylpyrrolidine and *o*-phenylenediamine in the same way as the former substance, with the only exception that a more concentrated solution of acetic acid must be used on account of the fact that this diketone is less soluble than diketodiphenylpyrroline. The phenazine is moderately soluble in boiling alcohol, and, on cooling the solution, slowly separates in yellow needles, which melt at 258°:

0.1833 gave 0.5532 CO<sub>2</sub> and 0.0965 H<sub>2</sub>O. C=82.30; H=5.24.

0.1784 " 19.4 c.c. N<sub>2</sub> at 17° and 762 mm. N=12.62.

C<sub>23</sub>H<sub>17</sub>N<sub>3</sub> requires C=82.38; H=5.07; N=12.54 per cent.

*Action of o-Phenylenediamine on 2:3 Diketodiacetyl-4-phenyl-5-methylcyclopentene.*

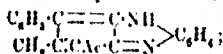
On adding to the red diketocyclopentene derivative, C<sub>14</sub>H<sub>12</sub>O<sub>2</sub> (1 gram), dissolved in hot alcohol or acetic acid, *o*-phenylenediamine (0.5 gram), the whole sets to a mass of dark coloured crystals. The product of the reaction is almost insoluble in alcohol, but dissolves in boiling glacial acetic acid, from which it crystallises in bunches of purple needles, softening at 245° and melting at 250°:

0.1782 gave 0.5225 CO<sub>2</sub> and 0.0855 H<sub>2</sub>O. C=79.97; H=5.33.

0.1720 " 14.2 c.c. N<sub>2</sub> at 21° and 747 mm. N=9.23.

C<sub>20</sub>H<sub>14</sub>ON<sub>2</sub> requires C=80.00; H=5.33; N=9.33 per cent.

The substance dissolves in cold concentrated sulphuric or hydrochloric acids to yield purple solutions. It has been pointed out before (p. 1439) that this compound must be represented thus:



It may be called *isophenylmethylacetylcyclopentene-phenazine*.

With phenylmercaptan, the diketocyclopentene derivative, C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>, unites to yield the additive compound, C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>S. This is formed when the diketone (0.5 gram), dissolved in hot alcohol, is mixed with phenylmercaptan (0.3 gram). The red colour of the solution changes to yellow, and, on adding water until turbidity is produced, yellow prisms separate, which soften at 125° and melt at 130° to a red liquid:

0.2344 (dried in a vacuum) gave 0.1650 BaSO<sub>4</sub>. S=9.67.

C<sub>20</sub>H<sub>14</sub>O<sub>2</sub>S requires S=9.47 per cent.

*Action of p-Nitrosodimethylaniline on  $\alpha$ -Hydrindone.*

$$\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \\ | \\ \text{CO} - \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \end{array} \cdot \text{H}_2\text{O}.$$

5 C

*Phenyl-p-tolylpyrrolinophenazine.*

This is prepared from diketophenyl-p-tolylpyrrolidine and  $\alpha$ -phenylenediamine in the same way as the former substance, with the only exception that a more concentrated solution of acetic acid must be used on account of the fact that this diketone is less soluble than diketodiphenylpyrrolidine. The phenazine is moderately soluble in boiling alcohol, and, on cooling the solution, slowly separates in yellow needles, which melt at  $258^\circ$ :

0.1833 gave 0.5532  $\text{CO}_2$  and 0.0865  $\text{H}_2\text{O}$ .  $\text{C}=82.30$ ;  $\text{H}=5.24$ .

0.1788 " 19.4 c.c.  $\text{N}_2$  at  $17^\circ$  and 762 mm.  $\text{N}=12.62$ .

$\text{C}_{22}\text{H}_{17}\text{N}_4$  requires  $\text{C}=82.34$ ;  $\text{H}=5.07$ ;  $\text{N}=12.54$  per cent.

*Action of  $\alpha$ -Phenylenediamine on 2,3-Diketocyclopent-4-phenyl-5-methylcyclopentene.*

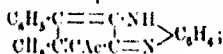
On adding to the red diketocyclopentene derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_2$  (1 gram), dissolved in hot alcohol or acetic acid,  $\alpha$ -phenylenediamine (0.5 gram), the whole sets to a mass of dark coloured crystals. The product of the reaction is almost insoluble in alcohol, but dissolves in boiling glacial acetic acid, from which it crystallises in bunches of purple needles, softening at  $21^\circ$  and melting at  $250^\circ$ :

0.1782 gave 0.5225  $\text{CO}_2$  and 0.0855  $\text{H}_2\text{O}$ .  $\text{C}=79.97$ ;  $\text{H}=5.33$ .

0.1720 " 14.2 c.c.  $\text{N}_2$  at  $21^\circ$  and 747 mm.  $\text{N}=9.23$ .

$\text{C}_{10}\text{H}_{14}\text{ON}_2$  requires  $\text{C}=80.00$ ,  $\text{H}=5.33$ ;  $\text{N}=9.33$  per cent.

The substance dissolves in cold concentrated sulphuric or hydrochloric acids to yield purple solutions. It has been pointed out before (p. 1439) that this compound must be represented thus:



It may be called *isophenylmethylacetylcyclopentenphenazine*.

With phenylmercaptan, the diketocyclopentene derivative,  $\text{C}_{11}\text{H}_{12}\text{O}_2$ , unites to yield the additive compound,  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{C}_6\text{H}_5\text{S}$ . This is formed when the diketone (0.5 gram), dissolved in hot alcohol, is mixed with phenylmercaptan (0.3 gram). The red colour of the solution changes to yellow, and, on adding water until turbidity is produced, yellow prisms separate, which soften at  $125^\circ$  and melt at  $130^\circ$  to a red liquid:

0.2344 (dried in a vacuum) gave 0.1650  $\text{BaSO}_4$ .  $\text{S}=9.67$ .

$\text{C}_{14}\text{H}_{12}\text{O}_2\text{S}$  requires  $\text{S}=9.47$  per cent.

This compound, like the product of the union of dihydrodiphenylpyrrone with phenylmercaptan, readily decomposes into its constituents, the diketone and the mercaptan.

*Action of p-Nitrosodimethylaniline on  $\alpha$ -Hydrindone.*

$\alpha$ -Hydrindone was prepared by the action of aluminium chloride on phenylpropionyl chloride, according to the method elaborated by Kipping (Trans., 1894, 65, 484), and the yield was found to be the same as stated by this author, if his directions are closely followed. The action of nitrosodimethylaniline on the hydrindone takes place under the influence of alcoholic potassium hydroxide, and is accompanied by development of heat. After several experiments, the following mode of procedure was adopted as giving the best results. The hydrindone (6 grams) and nitrosodimethylaniline (24 grams), dissolved in equal volumes of alcohol (about 50 c.c.), are mixed, the solution is cooled by ice, and gradually treated with a small quantity of alcoholic potassium hydroxide. The mixture soon turns deep brown and deposits a black solid; after being kept for 24 hours at the ordinary temperature, the reaction is complete. The solid is collected, washed with cold alcohol, and dissolved in boiling concentrated spirit (about 2.5 litres are required); on cooling, beautiful green prisms (9 to 9.5 grams) separate from the bluish-black solution, which, after a second crystallisation from the same solvent, melt and decompose at  $174^{\circ}$ :

0.1863 gave 0.4960  $\text{CO}_2$  and 0.1020  $\text{H}_2\text{O}$ . C = 72.65; H = 6.08.

0.1948 " 0.5194  $\text{CO}_2$  " 0.1045  $\text{H}_2\text{O}$  C = 72.73; H = 5.96.

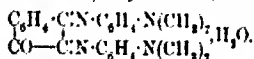
0.1890 " 21.8 c.c.  $\text{N}_2$  at  $18^{\circ}$  and 761 mm. N = 13.33.

0.1895 " 22.2 c.c.  $\text{N}_2$  "  $21^{\circ}$  " 765 mm. N = 13.41.

$\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_4$  requires C = 72.46; H = 6.28; N = 13.56 per cent.

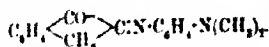
It will be noticed that the agreement between the analytical and theoretical numbers is not so close as might be desired, and that, specially, the percentage of hydrogen was found lower than required by the formula. On account of this discrepancy, I have frequently analysed this compound after repeated crystallisations, but without arriving at results which differ appreciably from those stated above.

The substance  $\text{C}_{22}\text{H}_{20}\text{O}_2\text{N}_4$  may be regarded as the hydrate of 1:3-bis(p-dimethylaminoanilo)- $\alpha$ -hydrindone.



It is only sparingly soluble in alcohol, moderately so in hot benzene, but does not readily crystallise from this solution without the addition of alcohol; it dissolves with great ease in glacial acetic acid to yield an indigo-blue solution, which, in a short time, changes

to yellow, and finally, if warmed, becomes reddish brown. The dark brown filtrate from the compound  $C_{15}H_{22}O_4N_2$ , when kept for a few days, deposits a very small quantity of a yellowish-red solid. This is moderately soluble in boiling alcohol to form a red solution, from which, on cooling, dark red crystals separate. These have a bluish-green, metallic lustre, and melt at  $238^\circ$ . As mentioned before, the substance is most probably the *p*-dimethylaminoacid of *α*-hydrindene,

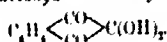


The following analysis indicates that it is not quite pure:

0.1910 gave 0.5318  $\text{CO}_2$  and 0.1100  $\text{H}_2\text{O}$ .  $\text{C} = 76.36$ ;  $\text{H} = 6.39$ .

$C_{15}H_{22}ON_2$  requires  $\text{C} = 77.27$ ;  $\text{H} = 6.06$  per cent.

*Triketohydrindene Hydrate.*



Dilute sulphuric acid attacks the compound  $C_{25}H_{32}O_4N_2$ , even at the ordinary temperature, but more readily on slightly warming on the water bath; the green crystals disappear, and a dark solution is produced which contains the hydrate of triketohydrindene. Owing to the fact that it is moderately soluble in cold, readily so in boiling, water, but sparingly so in ether, its isolation is rather troublesome. It was found necessary to shake the deep brown liquor which is formed by the action of the acid on the condensation product (10 grams) twenty times with fresh quantities of ether to extract the triketone hydrate (3.2 grams) which was formed. The red, ethereal extracts are decolorised with animal charcoal and evaporated on the water bath, when a yellow oil is left which solidifies on stirring with a glass rod. The solid readily dissolves in hot water, and, on cooling the concentrated solution, crystallises in colourless prisms, which turn red at  $125^\circ$ , froth at  $139^\circ$ , and melt and decompose at  $239$ – $240^\circ$ . The compound, after drying in a vacuum desiccator over sulphuric acid, gave the following results.

0.2083 gave 0.4637  $\text{CO}_2$  and 0.0640  $\text{H}_2\text{O}$ .  $\text{C} = 60.71$ ;  $\text{H} = 3.41$ .

$C_9H_6O_3$  requires  $\text{C} = 60.67$ ;  $\text{H} = 3.37$  per cent.

The aqueous solution of this substance colours the skin purple; this is similar to the behaviour of alloxan, which, in constitution, shows a certain resemblance to triketohydrindene. This substance reduces Fehling's solution as well as ammoniacal silver solution.

### *Action of Ammonia on Triketohydrindene.*

If the solution of triketohydrindene in dilute ammonia is kept for a short time, it becomes reddish-violet, and no longer reduces silver nitrate. On the addition of dilute hydrochloric acid to the ammoniacal solution, a red, gelatinous precipitate is formed.

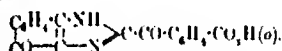
This is insoluble in water, sparingly soluble in ether, readily so in hot glacial acetic acid, moderately so in boiling alcohol, and, on cooling the alcoholic solution, crystallises in scarlet prisms. On heating, their colour changes to yellow at about  $245^{\circ}$ , and above  $330^{\circ}$  they melt to a dark liquid:

0.1910 gave 0.4760  $\text{CO}_2$  and 0.0540  $\text{H}_2\text{O}$ .  $\text{C} = 67.96$ ;  $\text{H} = 3.14$ .

0.2013 „ 15.6 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 758 mm.  $\text{N} = 8.83$ .

$\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2$  requires  $\text{C} = 67.92$ ;  $\text{H} = 3.14$ ;  $\text{N} = 8.80$  per cent.

As mentioned above (p. 1442), the compound is most probably so represented thus:

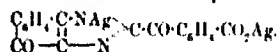


It dissolves in ammonia, potassium hydroxide, or sodium carbonate to yield reddish-violet solutions, which do not reduce silver nitrate or alkaline copper oxide solutions. The deep violet silver compound which it forms on the addition of silver nitrate to its solution in ammonia (containing only a slight excess of the base) is characteristic. If the solution is hot, a curdy, violet precipitate is produced, which is insoluble in water, and can be dried in the water-bath without undergoing any change:

0.2168 gave 0.0880 Ag.  $\text{Ag} = 40.59$ .

$\text{C}_{10}\text{H}_8\text{O}_4\text{N}_2\text{Ag}_2$  requires Ag 40.60 per cent.

In the light of the view expressed above concerning the constitution of the condensation product of the triketone with ammonia, the formula of the silver salt is to be expressed thus:



### *Action of Aniline on Triketohydrindene.*

Aniline reacts with the triketone as readily as does ammonia, and yields a yellow compound which separates in needles on bringing the aqueous solution of the triketone into contact with the base. This substance, however, is very unstable, it darkens at  $78^{\circ}$ , melts indefinitely at  $97^{\circ}$ , and, on heating with alcohol, suffers a change which is indicated by a deep violet coloration of the solution. I have not yet further examined this reaction.



*Action of Potassium Hydroxide on Triketohydrindene.*

If potassium hydroxide (containing about 15 per cent. KOH) is added to the triketone, the crystals turn yellow, and then dissolve to yield a solution which, at first, is yellow, but, on keeping for a short time at the ordinary temperature, becomes colourless. The result is, however, different if one does not wait until the last change occurs, but warms at once after the addition of the alkali to the triketone, under these conditions, a deep blue solution is formed, which retains its colour even on boiling, but becomes colourless on dilution with water, and then does no longer reduce alkaline copper oxide. The interpretation of this remarkable phenomenon I hope to be able to give in my next paper on triketohydrindene.

*Diphenylhydrazone of Triketohydrindene,  $C_{11}H_8O(N \cdot NH \cdot C_6H_5)_2$ .*

This compound is formed on adding phenylhydrazine to the solution of the triketone in acetic acid; after a short time, a red crystalline solid separates, which dissolves in a large quantity of boiling alcohol, and, on cooling, crystallises in orange needles, melting at  $207-208^\circ$ :

0.1737 gave 0.4517  $CO_2$  and 0.0735  $H_2O$ .  $C = 74.06$ ;  $H = 4.70$ .

0.1738 „ 25.2 c.c.  $N_2$  at  $19^\circ$  and 755 mm.  $N = 16.56$ .

$C_{11}H_8ON_2$  requires  $C = 74.12$ ;  $H = 4.70$ ;  $N = 16.47$  per cent.

The dihydrazone dissolves in cold concentrated sulphuric acid to yield a deep brown solution, which turns indigo-blue on the addition of a trace of potassium dichromate.

*Diemicarbazone of Triketohydrindene,  $C_{11}H_8O(N \cdot NH \cdot CO \cdot NH_2)_2$ .*

On mixing aqueous solutions of the triketone (1 gram) and semicarbazide hydrochloride (2 grams), an orange coloration is produced, and a yellow solid soon begins to separate. The reaction is complete after keeping the mixture at the ordinary temperature for a day. The substance is sparingly soluble in water or alcohol, and crystallises from these solutions in microscopic, yellow needles, which darken at  $175^\circ$  and melt at  $208^\circ$  with evolution of gas:

0.1630 gave 43.4 c.c.  $N_2$  at  $20^\circ$  and 758 mm.  $N = 30.55$ .

$C_{11}H_{10}O_2N_2$  requires  $N = 30.66$  per cent.

*Action of Hydroxylamine on Triketohydrindene.*

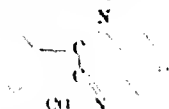
This reaction takes place if the aqueous solution of the mixture of triketohydrindene hydrate (1 gram) and hydroxylamine hydro-

chloride (3 grams) is kept at the ordinary temperature; a white solid is gradually formed, and after three days the separation is complete. The solid is sparingly soluble in water or alcohol, but separates very slowly from these solutions in the form of an amorphous powder, which dissolves in potassium hydroxide to yield a red solution, and melts at  $174^{\circ}$  with rapid evolution of gas. This product is a mixture of oximino-derivatives of triketohydrindene; its chief constituent is the trioxime,  $C_9H_5(NOH)_3$ ; this is indicated by the following analysis:

0.1875 gave 30.8 c.c.  $N_2$  at  $20^{\circ}$  and 755 mm.  $N = 18.66$ .

$C_9H_5O_3N_3$  requires  $N = 20.49$  per cent.

*Ketohydrindenophenazine,*



On mixing equal weights of triketohydrindene hydrate and phenylenediamine, dissolved in hot dilute acetic acid, a yellow solid is precipitated. This is sparingly soluble in cold, moderately so in boiling, alcohol, and, on cooling, crystallises in yellow prisms, which melt at  $218-219^{\circ}$ . The yield is almost theoretical:

0.1950 gave 0.5550  $CO_2$  and 0.0635  $H_2O$ .  $C = 77.62$ ;  $H = 3.62$ .

0.1755 .. 18.8 c.c.  $N_2$  at  $24^{\circ}$  and 767 mm.  $N = 12.13$ .

$C_{15}H_8ON_2$  requires  $C = 77.59$ ;  $H = 3.45$ ;  $N = 12.07$  per cent.

In conclusion, I may state that I am continuing the research on triketohydrindene as well as the study of the cyclic diketonic compounds which stand in a close relation to isatin.

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CAMBRIDGE.

### CXXXIII.—*The Constitution and Mutarotation of Sugar Anilides.*

By JAMES COLQUHOUN IRVING and DAVID McNICOLL, M.A., B.Sc.  
(Carnegie Scholar).

Is continuation of previous work (Trans., 1908, 93, 1429; 1909, 95, 1545) on the rotatory powers and constitution of sugar derivatives containing nitrogen, we have prepared and examined

the anilides of tetramethyl mannose, tetramethyl galactose, and trimethyl rhamnose, each of which has been obtained crystalline in forms which exhibit extensive mutarotation. These new compounds may prove useful in the identification of the parent sugars, as, whilst the latter are syrups, the anilides are readily crystallised, and their melting points lie far apart. For comparison, the anilides of the corresponding unsubstituted sugars have been re-examined, and these compounds have also been isolated in mutarotatory forms. As attempts to prepare anilides from tetramethyl fructose and trimethyl arabinose have, so far, resulted in the formation of syrupy products, these compounds are not included in the present paper.

The optical behaviour of the compounds described, and the rotatory changes observed in the course of their formation show that they are comparable with glucosyanilide and tetramethyl glucosyanilide, and it would thus appear that the glucosidic structure suggested for the latter compounds can be generally applied to the anilides of the sugar group. Owing to the ready hydrolysis undergone by such compounds, experimental evidence bearing directly on their constitution is difficult to obtain, but we have been able to apply the silver oxide reaction to the alkylated anilides now described, and find that in each case the compounds resist the methylating effect of the reagent completely. This result is consistent with the idea that the compounds in question are  $\gamma$ -oxides. It should be stated that several cases are now known in which the silver oxide reaction is not effective in alkylating hydroxyl groups, and thus negative results obtained in this way must be applied with caution in determining hydroxyl contents with a view to establishing constitution, particularly where tertiary groups are concerned. From unpublished results obtained in this laboratory, it would appear that ditertiary glycols are either not affected or give only monomethyl ethers (see also McKenzie and Wren, *Trans.*, this vol., p. 476), and another example in which the reagent gives a negative result is quoted by Meldola and Hay (*Trans.*, 1909, 95, 1379) in the case of a substituted phenol. In the present instance, however, the results obtained by the process are apparently valid, as, in the event of the compounds in question belonging to the aldehydic type, they would contain an unsubstituted secondary alcohol group in the  $\gamma$ -position. Such groups are known to undergo normal alkylation where the requisite solubilities are available, and as we find that mannitol is completely methylated by this reaction, there is thus evidence that all secondary alcohol groups in the sugar residues, irrespective of their position in the carbon chain, may be estimated by this process. The possibility of analysing other

anilides is practically excluded, as the compounds are hydrolyzed with extreme ease, in some cases even by heating with 90 per cent. alcohol, or with unpurified ether.

The details of the mutarotations are included with the experimental part, and only the principal results are tabulated below, the figures being given to the nearest whole numbers.

*Mutarotation of Methylated and Unmethylated Anilides.*

	Mannose.	Galactose.	Rhamnose.	Glucose.
(a) Unsubstituted anilides ...	-172° → -84° (pyridine)	-87° → -7° (90% alcohol)	+157° → +77° (alcohol)	+10° → -53° (methyl alcohol)
(a) Methylated anilides ...	-96° → -39° (acetone)	-77° → +35° (acetone)	+138° → +7° (alcohol)	+224° → +67° (methyl alcohol)

\* Irvine and Gilmour, *loc. cit.*; Gilmour, *Proc.*, 1909, 25, 225.

Owing to solubility considerations it was necessary to make use of different solvents in determining the mutarotations, and thus accurate comparison of the results is impossible, but it will be seen that the optical changes shown by corresponding pairs of compounds are of the same order throughout, and that the unsubstituted anilides are thus brought into line with the  $\gamma$ -oxidic anilides prepared from the methylated sugars. A qualitative comparison of the optical effect on the parent sugars of glucoaniline formation respectively, and also of the influence of methylation on each class of compound, shows certain regularities which are summarised below. The rotatory power of the  $\alpha$ -form of the reducing sugar is taken as the basis of comparison, and the signs + and - represent an increase or decrease of specific rotation in the dextro-sense shown by the corresponding methylaldosides and in the maximum initial values of the anilides:

	Mannose.	Galactose.	Rhamnose.	Glucose.
Effect of anilide formation	-	-	+	-
" methylation on anilide	+	+	+	+
" $\alpha$ -methylaldoside formation	+	+	-	+
" methylation on $\alpha$ -methylaldoside	-	-	-	-

The effect of anilide formation is thus uniformly opposite to that due to  $\alpha$ -glucoaniline formation, and the same holds true for the effect of methylation on each type of compound. The mutarotatory anilides now examined thus closely resemble the  $\beta$ -methylglucosides so far as optical considerations are concerned.

## EXPERIMENTAL

*Tetramethyl Mannoscanilide.*

A 30 per cent. ethyl alcoholic solution of tetramethyl mannose (Trans. 1906, 67, 1462) (1 mol.) was boiled with an excess of aniline (8 mols) for three hours. After removal of the solvent and excess of the base by evaporation under diminished pressure, a dry, crystalline solid remained, which was recrystallized from petroleum of high boiling point. The *anilide*, which was thus obtained in almost quantitative amount, consisted of slender prisms, melting at 142–143°.

Found, C=61.51; H=8.19; OMe, 38.59.

$C_{17}H_{19}ON(OMe)_4$  requires C=61.74; H=8.04;

OMe=39.87 per cent.

The compound was readily dissolved in the cold by all ordinary organic solvents with the exception of light petroleum. Although perfectly stable when exposed in air, the compound was very easily hydrolyzed. Even boiling with commercial ether was sufficient to decompose it completely into its constituents. It was thus necessary to use specially purified reagents in the preparation and manipulation of the compound.

The optical changes shown by the compound in solution are greatly accelerated by the presence of traces of catalysts, and are not detectable unless special precautions are taken to clean the polarimeter tube and its accessories.

Solvent	$c$	Initial $[\alpha]_D^{20}$	Final $[\alpha]_D^{20}$
Methyl alcohol	2.161	87.9	-8.3*
Acetone	2.011	95.5	39.9

In the case of the solution in methyl alcohol, mutarotation proceeded spontaneously, and was generally complete in three to four hours. On the other hand, the acetone solution preserved a constant rotatory power until a trace of acid was added. Apparently a different equilibrium is established in the two solvents, judging from the greater difference shown by the end points as compared with the initial values.

*Mannoscanilide.*

The following process proved most effective for the rapid preparation of this compound. Fifteen grams of the sugar (1 mol.) were dissolved in boiling methyl alcohol, and 45 grams of aniline (6 mols.) were then added. The separation of the crystalline product commenced almost immediately, and after boiling for half an hour the reaction was complete. The yield was practically

quantitative, and the compound separated in the pure state, as repeated crystallization from boiling water had no effect on the melting point or specific rotation:

Found, C=56.30; H=6.98; N=5.41.

$C_{12}H_{17}O_5N$  requires C=56.47; H=6.67; N=5.49 per cent.

*Mannoseanilide* crystallizes in rectangular prisms, melting with complete decomposition at  $181^\circ$ . The compound is insoluble in all ordinary solvents, with the exception of pyridine and boiling water. The mutarotation observed in pyridine solution ( $c=2$ ) was  $[\alpha]_D^{25} -178.5^\circ \rightarrow -81.5^\circ$ .

In order to obtain, if possible, a specimen of the compound showing mutarotation in the opposite direction, the anilide was also prepared by the method of slow condensation in the cold. A 5 per cent. solution of mannose in 85 per cent. alcohol was prepared at the boiling point of the solvent, and kept for eight hours until the rotation at  $20^\circ$  was constant. Aniline (8 mols.) was then added, and polarimetric readings of the solution were taken, at first every few minutes and afterwards at intervals of fifteen minutes. The curve representing the optical changes showed a perfectly regular change from dextro to levo-rotation. Some of the results are appended:

Time, in minutes, from first reading	0	10	70	120	215
Specific rotation	$-23.7^\circ$	$18.0$	$-0.9^\circ$	$12.3$	$-81.4^\circ$

No further readings beyond the last mentioned were possible, as a quantity of the product suddenly crystallised in the polarimeter tube. The filtrate was now *dextro* rotatory, and the specific rotation, calculating  $c$  by subtracting the weight of sugar contained in the separated anilide from that originally present in solution, was now  $+24.0^\circ$ , a value equal to that observed at the beginning of the condensation. The same held true for the removal of subsequent crops of the product, the specific rotation of the mother liquor, calculated as above, always showing a return to the initial value, indicating that uncondensed sugar in the equilibrium condition was the only active constituent in the filtrate. This behaviour brings the condensation into line with the formation of the alkylmannosides, where, similarly, only one stereoisomeride is produced. All the crops of the anilide had the same melting point ( $181^\circ$ ), and showed the same mutarotation in pyridine solution:

	Initial $[\alpha]_D^{25}$		Final $[\alpha]_D^{25}$
First crop	$-171.8$	$\rightarrow$	$-82.0^\circ$
Final "	$171.0$	$\rightarrow$	$81.2$

There is thus evidence for the production of only one form of mannoseanilide irrespective of whether the condensation is conducted slowly in ethyl alcohol or at the boiling point of methyl

alcohol, and although mutarotation indicates the existence of a second form, all attempts failed to isolate this monomer or a mixture of the two forms showing downward mutarotation in the anisotropic state. A solution in pyridine, which had attained the constant specific rotation  $-81.5^\circ$  when evaporated to dryness under diminished pressure, yielded the equilibrium mixture  $[\alpha]_D^{25} = -81.6^\circ$  in the crystalline state. When heated with solvents, this was rapidly converted into the mutarotatory *levo*-form.

**Tetramethyl Galactosaminide.**

This compound, prepared from tetramethyl galactose (Irvine and Cameron, Trans. 1904, 85, 1071), is sparingly soluble in ethyl alcohol, from which it separates in rectangular prisms, melting at 19°. The yield is quantitative:

Found, C = 61.60; H = 8.30; OMe = 38.65.

$C_{17}H_{13}ON(OMe)_4$  requires C=61.74; H=8.04;

OMe 39.87 per cent.

The compound resembled the other alkylated anilides examined, with the exception that it is much more sparingly soluble in the usual solvents. The optical rotations were accordingly observed in acetone solution at 30°. The mutarotation then observed in a 1 per cent. solution was  $[\alpha]_D^{25} - 77.1^\circ \rightarrow +37.5^\circ$ .

*Galactosylamide.*

Sorokin (*J. Russ. Phys. Chem. Soc.*, 1886, 18, 129) describes the preparation of this compound, and states that it melts at 147°. Various specific rotations for the substance are quoted, the value  $-33.1^{\circ}$  being given for methyl alcohol, and  $-31.3^{\circ}$  for a solution in 90 per cent. ethyl alcohol. These values are now corrected.

A 6 per cent. solution of galactose (1 mol.) in 90 per cent. ethyl alcohol, containing excess of aniline (5 mols.), was prepared at the boiling point of the solvent. When the sugar had completely dissolved, the solution was concentrated to half volume and precipitated with dry ether. Galactoseanilide was thus obtained in good yield, and, after recrystallisation from dilute alcohol, the compound melted with slight decomposition at 151°. Mutarotation was only detected with difficulty, as the compound is sparingly soluble, and in the preparation of the solutions for observation of the rotatory power, gentle warming of the solvent is necessary so that readings may be taken without delay:

Solvent	c.	Initial $\eta_{sp}/c$	Final $\eta_{sp}/c$
80 per cent. ethyl alcohol	2.325	86.9	6.88
90 " "	2.394	88.5	6.97
Methyl alcohol	0.507	76.9	31.60

The low concentration used in the case of the methyl-alcoholic solution is explained by the fact that in this case solution was effected in the cold. With  $c = 1.667$ , the solvent had to be warmed before solution was complete, and practically no mutarotation was detected. It is thus evident that the specific rotations previously found for this substance are reliable only so far as the permanent value in methyl alcohol is concerned. On the other hand, the rotations quoted in the literature for ethyl-alcoholic solutions evidently represent intermediate values observed before mutarotation was complete.

The progress of the condensation of galactose with aniline was followed, as usual, polarimetrically, the customary excess of anilide being added to a 5 per cent. solution of the sugar in 65 per cent. alcohol. The condensation at first proceeded very rapidly, and after six hours the solution was levorotatory. The rotation became constant after eight days, but as the curve representing the optical changes was perfectly regular, no indication was obtained of the formation of the dextrorotatory form of the anilide.

#### *Trimethyl Rhamnoseanilide.*

This compound was readily obtained from trimethyl rhamnose by the method already described for the preparation of tetramethyl mannosanilide. The product was recrystallised from light petroleum, and was then obtained in needles, melting at  $111-113^\circ$ .

Found,  $C = 63.90$ ;  $H = 8.21$ ;  $OMe = 32.5$ .

$C_{27}H_{44}ON(OMe)_3$  requires  $C = 64.01$ ;  $H = 8.25$ ;  $OMe = 33.1$  per cent.

The compound displayed the usual solubilities of alkylated anilides, was very easily hydrolysed, and showed extensive mutarotation;

Solvent.	$c$ .	Initial $[\alpha]_D^{25}$ .	Final $[\alpha]_D^{25}$ .
Ethyl alcohol .....	1.1840	+138.5	+16.7
Acetone .....	1.2150	135.3	46.9

From the identity of the initial rotations and the divergence shown by the permanent values, it would appear that a different equilibrium is attained in the two solvents.

#### *Rhamnoseanilide.*

This compound has already been prepared by Rayman and Krain (Bull. Soc. chim., 1887, [ii], 48, 463), who describe it as melting at  $118^\circ$ . No rotation values are quoted, the statement merely being made that the compound is dextrorotatory. A 20 per cent. ethyl-alcoholic solution of anhydrous rhamnose was boiled with aniline (5 mol.) for one and a-half hours, the product being isolated as



in the case of mannosanilide. The anilide was crystallized from a mixture of alcohol and light petroleum, and consisted of rectangular prisms, melting at  $144^{\circ}$ :

Found, C = 60.15; H = 7.32; N = 5.74.

$C_{12}H_{11}O_2N$  requires C = 60.25; H = 7.32; N = 5.85 per cent.

The observed mutarotation in absolute alcohol was  $[\alpha]_D^{25} + 95.8^{\circ} \rightarrow 76.0^{\circ}$ . Recrystallization from ethyl acetate effected a better separation of the mutarotatory forms, the maximum rotation changes then observed being  $[\alpha]_D^{25} + 136.2^{\circ} \rightarrow 77.1^{\circ}$ . Experiments conducted with the object of separating the form showing the converse change gave negative results.

*Polarimetric Examination of the Condensation.*—All the materials used were anhydrous, and precautions were taken to prevent the access of moisture during the process. This was necessary to prevent the optical changes being complicated by the addition of water to the anhydrous sugar. An 8 per cent. solution of dry rhainose in absolute ethyl alcohol containing 24 per cent. of aniline was prepared at  $20^{\circ}$  and kept in the dark. The initial specific rotation, calculated on the weight of sugar present, was  $-5.4^{\circ}$ . In one hour the solution was dextrinotatory, and in forty-eight hours the process was complete. The curve representing the optical changes was regular, and this was also the case when the reaction was carried out at  $50^{\circ}$  with a more concentrated solution of the sugar (20 per cent.). In each case, however, the curve indicated that the form showing upward mutarotation in the dextro sense was the first to be produced.

We take this opportunity of expressing our indebtedness to the Carnegie Trust for a research grant in aid of the investigation.

CHEMICAL RESEARCH LABORATORY,  
UNION COLLEGE OF ST. SALVATOR AND ST. LEONARD,  
UNIVERSITY OF ST. ANDREWS.

#### CCXXXIV.—Condensations of Phenanthraquinone with Ethyl Malonate and Ethyl Acetoacetate.

By MARION BROCK RICHARDS (Carnegie Scholar in the University of Aberdeen).

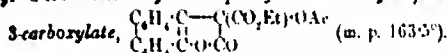
JAPP AND WOOD (Trans., 1905, 87, 712) described some condensations of phenanthraquinone with ketonic compounds under the influence of acetic anhydride containing a little concentrated sulphuric acid.

The condensation products of phenanthraquinone with ethyl malonate and with ethyl acetoacetate, of which mention was made in that paper, have now been further investigated.

*Condensation of Phenanthraquinone with Ethyl Malonate.*

Fifty grams of finely powdered phenanthraquinone (free from anthraquinone\*), 100 grams of ethyl malonate, 200 grams of acetic anhydride, and 30 grams of concentrated sulphuric acid were heated to 50° for seven days.† The crystals which had separated, and the mother liquor, each yielded a condensation product.

*Ethyl 2-Keto-3-acetoxy-4:5-diphenylenc-2:3-dihydrofuran-*

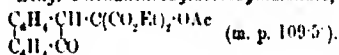


The foregoing crystals, after recrystallisation from alcohol, yielded white, glistening scales, melting at 163.5°. From benzene, on the addition of light petroleum, the substance crystallised in clusters of flat needles. The yield was 29 grams:

0.2036 gave 0.5148 CO<sub>2</sub> and 0.0800 H<sub>2</sub>O. C = 68.96; H = 4.37.

C<sub>21</sub>H<sub>14</sub>O<sub>6</sub> requires C = 69.23; H = 4.40 per cent.

*Ethyl Phenanthroxylacetoxy-malonate,*



The acetic anhydride mother liquor, after treatment with water and alcohol, yielded a substance which crystallised from ether in large, white, lustrous prisms, and from alcohol partly in prisms and partly in fine needles, each form melting at 109.5°:

0.2013 gave 0.4963 CO<sub>2</sub> and 0.0973 H<sub>2</sub>O. C = 67.24; H = 5.37.

C<sub>22</sub>H<sub>16</sub>O<sub>7</sub> requires C = 67.32; H = 5.37 per cent.

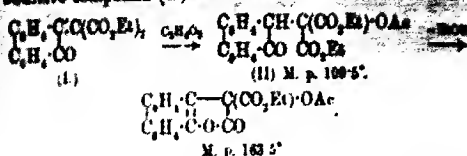
When this substance was treated at 50° with the mixture of acetic anhydride and sulphuric acid, white crystals separated, which after recrystallisation from alcohol melted at 163.5°, and were identified by a mixed melting point test as the foregoing compound, C<sub>22</sub>H<sub>16</sub>O<sub>7</sub>, showing that the present compound is an intermediate stage in the formation of the previous one.

The formation of these compounds may be explained on the assumption that the unknown ethyl phenanthroxylenemalonate (I)

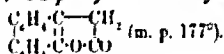
\* The phenanthraquinone used for these reactions must be purified by means of the sodium hydrogen sulphite compound, as some of the products are almost impossible to separate from the anthraquinone which will otherwise contaminate them.

† If the usual proportion of sulphuric acid is employed, namely, 3 grams of acid to 100 grams of acetic anhydride, the condensation takes much longer.

is first formed; this compound then unites with acetic acid, and the additive compound (II) loses alcohol:



2 Keto-4,5 diphenylene-2:3 dihydrofuran,

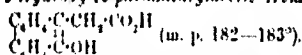


Fifteen grams of the substance  $\text{C}_{27}\text{H}_{20}\text{O}_6$  (m. p.  $163.5^\circ$ ), 12 grams of red phosphorus, and 100 grams of hydriodic acid (D 1.7) were boiled together for four hours under reflux. The solid substance was extracted first with ether, and, on evaporating off the ether, a small quantity of substance was obtained which crystallized from benzene in needles. The residue was then extracted with boiling benzene, and from this extract there separated clusters of long, silky, colourless needles, melting at  $177^\circ$ . The yield was about 8½ grams:

0.1476 gave 0.4447  $\text{CO}_2$  and 0.0575  $\text{H}_2\text{O}$ .  $\text{C}=82.17$ ;  $\text{H}=4.33$ .

$\text{C}_{16}\text{H}_{10}\text{O}_2$  requires  $\text{C}=82.05$ ;  $\text{H}=4.27$  per cent.

9-Hydroxy-10 phenanthrylacetic Acid,



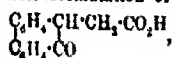
The lactone was dissolved in aqueous potassium hydroxide on the water-bath, the solution acidified with hydrochloric acid, and the precipitated acid collected and dried at  $100^\circ$ . The yield was quantitative. The acid was difficult to purify by recrystallisation, as the solutions very readily oxidised, turning green or orange coloured. For analysis it was crystallised from a mixture of acetone and benzene, from which it was obtained in colourless prisms. It melted, when rapidly heated, at  $182-183^\circ$ .

0.1839 gave 0.5133  $\text{CO}_2$  and 0.0801  $\text{H}_2\text{O}$ .  $\text{C}=75.98$ ;  $\text{H}=4.84$ .

$\text{C}_{16}\text{H}_{12}\text{O}_3$  requires  $\text{C}=76.19$ ;  $\text{H}=4.76$  per cent.

Boiling with acetic anhydride reconverted the acid into the lactone.

In view of the possible formulation of the acid as



the action of hydrotolamine was tried, but no uric acid was obtained.

That the acid contains a phenolic hydroxyl group is shown by the fact that the monopotassium salt, which is sparingly soluble in water, readily dissolves in excess of potassium hydroxide, doubtless yielding the dipotassium salt. From this solution carbon dioxide reprecipitates the monopotassium salt.

The salts of the acid, like the acid itself, decomposed very readily. The silver salt turned dark soon after it was precipitated, whilst the sodium and barium salts decomposed when attempts were made to recrystallise them, and had therefore to be analysed direct.

*Barium Salt.*—This salt was prepared by precipitating the ammonium salt with barium chloride. It was dried in the air:

0.3958 lost, at  $110^{\circ}$ , 0.0406  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O} = 10.26$ .

$(\text{C}_{14}\text{H}_{11}\text{O}_5)_2\text{Ba} \cdot 4\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 10.13$  per cent.

0.3552 anhydrous salt gave 0.1324  $\text{BaSO}_4$ .  $\text{Ba} = 21.93$ .

$(\text{C}_{14}\text{H}_{11}\text{O}_5)_2\text{Ba}$  requires  $\text{Ba} = 21.48$  per cent.

*Sodium Salt.*—This salt was prepared by boiling the acid with a solution of sodium carbonate. It crystallised in fine needles, and was dried at  $110^{\circ}$ :

anhydrous salt gave 0.0995  $\text{Na}_2\text{SO}_4$ .  $\text{Na} = 8.25$ .

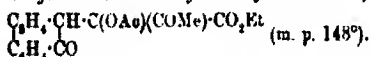
$\text{C}_{14}\text{H}_{11}\text{O}_5\text{Na}$  requires  $\text{Na} = 8.39$  per cent.

#### *Condensation of Phenanthraquinone with Ethyl Acetoacetate.*

The condensation of phenanthraquinone with ethyl acetoacetate in the presence of dilute aqueous potassium hydroxide has already been studied by Japp and Streatfield (Trans., 1883, 43, 28) and Japp and Klingemann (Trans., 1891, 59, 1); but the results differ entirely from those obtained by the method here described.

Fifty grams of finely powdered phenanthraquinone, 80 grams of ethyl acetoacetate, 200 grams of acetic anhydride, and 6 grams of concentrated sulphuric acid were kept at about  $20^{\circ}$  for about a fortnight. The mixture was then filtered, 15 grams of a brown solid being obtained. At the slightly higher temperature of  $30^{\circ}$ , the yield is reduced to 5 grams.

#### *Ethyl 9-Phenanthroxylacetoxyacetoacetate,*



The brown solid was boiled with benzene, and the solution filtered from a small quantity of yellow, insoluble substance. The benzene solution deposited colourless prisms, which melted finally at  $148^{\circ}$ . These turned yellow on exposure to light:

0.1991 gave 0.5070  $\text{CO}_2$  and 0.0846  $\text{H}_2\text{O}$ .  $\text{C}=69.45$ ;  $\text{H}=5.28$ .

$\text{C}_{22}\text{H}_{14}\text{O}_4$  requires  $\text{C}=69.47$ ;  $\text{H}=5.36$  per cent.

*Compound,  $\text{C}_{22}\text{H}_{14}\text{O}_4$ .*—The sparingly soluble yellow substance was dissolved in solvent naphtha (b. p.  $164-170^\circ$ ), giving a yellow, fluorescent solution, from which there crystallised minute, yellow needles, which did not melt below  $315^\circ$ . On analysis it gave figures pointing to the formula  $\text{C}_{22}\text{H}_{14}\text{O}_4$ , but the combustion was not conclusive, as the substance left 13 per cent. of ash. Owing to the difficulty in obtaining the substance, no further preparation was made:

0.1313 gave 0.3494  $\text{CO}_2$  and 0.0550  $\text{H}_2\text{O}$ .  $\text{C}=72.57$ ;  $\text{H}=4.65$ .

$\text{C}_{22}\text{H}_{14}\text{O}_4$  requires  $\text{C}=72.93$ ;  $\text{H}=4.97$  per cent.

Ethyl phenanthroxyacetoxycetoacetate, when allowed to remain in the cold with the mixture of acetic anhydride and sulphuric acid, yielded the foregoing dehydration product,  $\text{C}_{22}\text{H}_{14}\text{O}_4$ ; hence the substance melting at  $143^\circ$  is an intermediate stage.

The action of the mixture of acetic anhydride and sulphuric acid at the ordinary temperature on Japp and Streatfeild's ethyl

phenanthroxylenecetoacetate,  $\text{C}_{22}\text{H}_{14}(\text{CO}_2\text{Me})\text{CO}_2\text{Et}$ , was also tried,  $\text{C}_{22}\text{H}_{14}\text{CO}$

but this yielded only the compounds  $\text{C}_{20}\text{H}_{14}\text{O}_3$  (m. p.  $26^\circ$ ) and  $\text{C}_{22}\text{H}_{14}\text{O}_3$  (m. p.  $165-171^\circ$ ), which Japp and Klingemann obtained by the action of acetic anhydride alone on this substance at  $150^\circ$  (Trans., 1891, 59, 15).

This research was carried out under Professor Japp's supervision, and the author wishes to thank him for the interest he has always taken in the work.

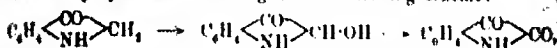
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UNIVERSITY OF AMSTERDAM.

## CXXXV.—Indirubin. Part I.

By WILLIAM POPPLEWELL BLOXAM and A. G. PERKIN.

It is well known that certain varieties of natural indigo contain a considerable quantity of indirubin, and it is probable (Trans., 1907, 91, 279) that at least a trace occurs in all samples of the natural dyestuff. That the indirubin originates from the indican existing in the leaves of the various species of the *Indigofera* which are employed in the manufacturing process, and is due to no second

constitution of the plant is now certain, and its production is to be explained in all cases as due to the condensation of isatin with indoxyl according to Baeyer's equation (*Ber.*, 1881, 14, 1745). Thus, it has been clearly shown (*Trans.*, 1909, 95, 830) that indigo containing indirubin can be readily produced from crystalline indican by a replica of the factory method, and again an important point in this respect has been the isolation of isatin itself from natural indigo rich in indirubin (*Proc.*, 1907, 23, 30). The formation of the necessary isatin is favoured by special circumstances, such as oxidation of the indoxyl by air in the presence of alkali or acid, and may also be affected to some extent by temperature. Again, the fact that indoxyl acid (*Trans.*, 1909, 95, 847) by air-oxidation is readily converted, at least in part, into isatin has been previously discussed, and may have some bearing upon the production of indirubin during the manufacturing process. It is most probable that this so-called "secondary" oxidation of the indoxyl proceeds according to the following scheme:



and that it is also indirectly the cause of the production of indigo brown (*loc. cit.*).

With a desire of studying in a quantitative manner the various conditions which are responsible for the formation of indirubin during the manufacture of natural indigo, samples of this dyestuff, which had been prepared in the laboratory from pure indican, were submitted to analysis by methods which are described as suitable for this purpose. The results were, however, not sufficiently accurate either in the case of these laboratory products or with specially prepared mixtures of the pure colouring matters, and it was thus necessary, before proceeding further with the main object of the inquiry, to devise, if possible, a method better suited to our requirements.

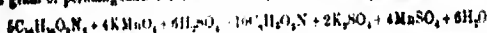
It is well known that indirubin is much more resistant to oxidation and reduction than indigotin, properties which also apply to the sulphonic acids of these colouring matters. When dealing therefore with the latter substances under usual analytical conditions, and employing either potassium permanganate\* or titanium chloride,\* the indigotin is to some extent preferentially attacked,

\* Experiments have indicated the correctness of Koppeschaar's statement; thus, when 20 c.c. of a solution of indigotin-sulphonic acid (1 gram per litre) was treated with potassium permanganate (1 gram per litre) under the conditions of concentration previously given by one of us (*J. Soc. Chem. Ind.*, 1906, 25, 735), 9 c.c. of the reagent were necessary for its decolorisation, but, on the other hand, for 20 c.c. of indirubinsulphonic acid of the same strength but 7.25 c.c. were required, although the oxidation in the latter case was of a slower character. Curiously enough, with

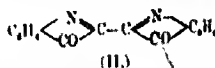
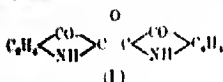
as then towards the end of the operation the solution consists entirely of indirubinsulphonic acid. In the case however

a mixture of equal parts of the two sulphonic acids, 25 c.c. in all, the total consumption of permanganate was greater than that required for the sum of the two constituents (Found, 10.45 c.c. Theory requires 10.17). Again the amount of reagent employed up to the disappearance of the blue coloration was 4.7 c.c. (theory requires 5.12 c.c.), so that these figures indicate that the original solution contained 66.5 per cent. of indigotin, 45.15 per cent. of indirubin, a total of 105.65 per cent. instead of the amounts above stated. It is evident, therefore, that the permanganate does not discriminate quantitatively between the blue and red sulphonic acids, and could not, therefore, be employed for this purpose, or for the estimation of the total quantity of mixed colouring matters present. The cause of the latter discrepancy originates from the slow oxidation of the indirubinsulphonic acid by the permanganate, which admits of the simultaneous further degradation of the decomposition products of the indigotin which have been produced at the earlier stage of the process.

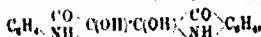
The action of potassium permanganate on solutions of the indigotinsulphonic acids is of interest, because the amount of the reagent necessary for the decoloration of the liquid varies, to some extent, with its concentration, and this point has been alluded to by Dawson (*A Dictionary of Dyes, mordants, etc.*, by Dawson, Gardner, and Laycock, 1901, 187). It has been found, for instance, at the concentration employed by one of us, and which is identical with that recommended by Badische Anilin- und Soda Fabrik (*Chemistry of Pure Indigo*, B.A.S.F. brochure, 1900), that, under these conditions, 1 gram of indigotin as sulphonic acid requires 0.45 gram of permanganate for decoloration, whereas the equation:



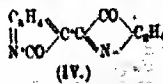
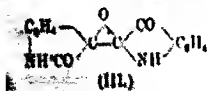
implies that 0.4824 gram of the reagent is necessary. It is evident, therefore, that this oxidation is of a complex nature, and either consists of two distinct stages, the formation of isatinsulphonic acid or of two distinct reactions involving the production of the two separate substances. As regards the first suggestion, it is possible that the isatin formation would be preceded by that of an intermediate compound (I), or that by the latter in addition to isatin, a dehydroindigotin



is formed. In case the first product of the reaction consists entirely of dehydroindigotin, this must prior to further oxidation to isatin take up two molecules of water with formation of dihydroxyindigotin,



but there is at present no evidence on this point. Very striking in this respect is the small amount of permanganate required for the decoloration of indirubinsulphonic acids, and a similar explanation is here available. Either, therefore, the compound (III) or the unknown dehydroindirubin (IV) is produced in the first



of the latter reaction, it has been stated by Koppeschaar (*Zeit. anal. Chem.*, 1899, 38, 1) that it is not possible to obtain trustworthy results with indigos in which some quantity of indirubin is present, and Rawson (*J. Soc. Chem. Ind.*, 1899, 18, 252), although not so emphatic on this point, considers that it is not easy in this manner to obtain accurate results. On the other hand, it is usual to separate the more soluble indirubin from the indigo by a process of extraction, and for this purpose ether (Rawson, *loc. cit.*), acetone (Gardner and Denton, *J. Soc. Dyers*), and acetic acid (Koppeschaar, *loc. cit.*) have been recommended. Rawson's statement that indirubin is easily soluble in ether can only apply to the crude commercial solvent, for it was ascertained by experiment that the pure liquid dissolves but a trace of this colouring matter. In a criticism of Rawson's process, Gardner and Denton (*loc. cit.*) state that the amount of indirubin estimated depends greatly on the length of time the extraction proceeds, and that even after three hours' boiling the indirubin is not completely extracted from the indigo. Experiments with this method fully corroborated the objections raised by the latter authors, and, moreover, the ethereal extract of the colouring matter prepared according to Rawson's directions was of a purple blue colour, and was not easily comparable with the standard solution of indirubin in ether. Curiously enough, pure acetone was found also to exert but little solvent action towards indirubin, and thus it appears evident that the active agent in both the so-called ether and acetone methods consists in reality of the alcoholic impurity which is present in the compound of its sulphonic acid. It is considered probable that the dehydroindigotin and dehydroindirubin formation occurs in these respective instances.

On the other hand, with titanium chloride, and employing the process according to the details previously given by one of us, it was found that this reagent behaves in an identical manner towards both indigotin- and indirubin-sulphonic acids, and that the consumption in each case is identical. Moreover, numerous trials carried out with mixtures of the pure sulphonated colouring matters indicated that the amount of the reagent required was, in all cases, equal to the sum of that theoretically necessary for each constituent. This is clearly indicated by the following results:

	Indigotin- disulphonic acid (c.c.).	Indirubin- disulphonic acid (c.c.).	Present, Indigotin + Indirubin, gram.	Found, indigotin + indirubin, gram.	Found, per cent.	
1	15	+	10	0.0260	0.02497	99.90
2	10	+	15	0.0250	0.02505	100.21
3	20	+	5	0.0250	0.02512	100.50
4	5	+	20	0.0250	0.02494	99.77

It was found, however, that it was not possible by means of this reagent to differentiate in a quantitative manner as to the amount of each of the sulphonated colouring matters which were present in the mixture. Although, during the reaction, the blue colour of the liquid disappears and a red stage is ultimately reached, this only occurs before the final transition to bright yellow.



merical liquids. Indeed, it is pointed out by Gardner and Denton that the quality of the acetone used is of importance.

It is probable therefore that the failure of experimenters to give satisfactory results by the use of the latter method was occasioned to some extent by the nature of the commercial acetone (Kahlbaum's) which was employed. Thus, the addition of the aqueous salt solution to the acetone extract of the indigo in the manner recommended by these authors for the precipitation of impurities unfortunately also caused the deposition of indirubin itself, and, on the other hand, it was observed that a precipitation of the dissolved indigotin from the acetone in this manner was far from complete. Finally, in regard to both the ether and acetone processes, no account is given by their authors of attempts to standardise their processes with mixtures of the pure colouring matters, and their accuracy does not therefore appear to have been submitted to experimental proof.

That indirubin can be completely extracted by means of boiling acetic acid has already been shown in a previous communication (*loc. cit.*), and on this account Gardner and Denton's statement (*loc. cit.*) that Koppeschaar's process is inconvenient on account of the apparent insolubility of the colouring matter in glacial acetic acid and the impossibility of completely extracting it from indigo is difficult to understand. Experiments with this method gave fairly satisfactory results, for, employing a mixture of 99 parts of pure indigotin and 1 part of indirubin, the actual figures obtained were indigotin 97.36, and indirubin 0.976 per cent. In carrying out the process, however, it was discovered that in addition to indirubin the acetic acid also removes a small quantity of indigotin from the indigo, and for trustworthy figures a standard acetic acid solution of the latter colouring matter in addition to that of indigotin is necessary. Considerable discomfort is, however, occasioned by the employment of the glacial acetic acid in open vessels, although it is probable that with certain modifications this and other minor objections to the method could be overcome.

It has been previously pointed out (*Trans.*, 1907, 91, 279) that pyridine is an excellent solvent for indirubin and also for indigo brown, whereas in regard to indigotin its power in this respect is very limited, and it thus appeared possible that an analytical method based on the employment of this liquid could be devised. A necessary feature of such a process was obviously to avoid the use of open

\* In this paper, the statement occurs that indigo-brown is soluble in acetone. As the main constituent of indigo-brown (*Trans.*, 1907, 91, 279) is practically insoluble in all solvents with the exception of pyridine, this can only refer to the share of the more soluble compound which is present in this mixture.

remains, and after repeated trials this was ultimately effected by the process described in the following pages.

The qualitative examination of indigo for indirubin is readily effected by digesting the finely-divided dyestuff for a few seconds with a small amount of boiling pyridine. Employing, for instance, a mixture of pure indigotin, 99 per cent., and pure indirubin, 1 per cent., a deep red extract was obtained in this manner, containing but a trace of blue, whereas with indigotin, 99.999 per cent., and indirubin, 0.001 per cent., the supernatant liquid was of a purple-red colour. In the case of natural indigos, the colour of the indirubin, if present in the pyridine extract in but limited amount, may be masked to some extent by the presence of indigo brown. To remove the latter, the pyridine solution is poured into a small quantity of methylated ether, and the mixture agitated with dilute sodium hydroxide solution. The ethereal layer will then possess the red colour which is characteristic of indigo red.

The following table indicates the selective action of various solvents at the boiling point on indirubin and indigotin respectively alone, and also on mixtures of these colouring matters in definite proportion:

Solvent	Indirubin.	Indigotin.	Indigotin, 99 per cent., indirubin, 1 per cent.	Indigotin, 99.999 per cent., indirubin, 0.001 per cent.
Pyridine .....	Deep currant-red	Intense blue	Deep currant-red	Purple-red
Acetic acid ....	Deep purple-red	Faint blue	Strong purple	Faint blue only
Acetone .....	Red, but less intense	Insoluble	Magenta, but less intense	Faint blue
Methylated ether	Faint reddish-yellow	Insoluble	Magenta, but again less intense	No trace of red

#### *The Pyridine Method.*

The finely sieved sample of the air-dried indigo (0.25 to 1 gram) is weighed out into a small beaker, and evenly incorporated with 30 to 30 grams of purified sand. A thin-walled glass tube, approximately 25 x 90 mm., and which, for the sake of convenience, will be referred to as the "container," is neatly closed at one end by means of cotton cloth, which is fastened to the tube with fine string or silk cord (copper or brass wire must not be employed).\*

\* In the earlier experiments, the cotton cloth was replaced with copper and brass gauze, and in these analyses a small, but persistent, loss of approximately 2 per cent. of indigotin occurred. This was eventually accounted for by the fact that the pyridine (chemical pure pyridine does not exert a deleterious effect) employed, and apparently all commercial varieties of this liquid, contain a little ammonia, and

and into this is introduced a layer of asbestos covering the sand, and about 1 cm. thick. With the aid of a Gattermann funnel, the contents of the beaker are now poured in, and the beaker is cleaned from adhering dyestuff by successive washings with sand, which are then added to the main bulk. Sufficient sand is then added to form a layer on the upper surface of the indigo mixture, and the whole is then loosely covered with asbestos, which can be previously employed if necessary to remove the last traces of indigo from the beaker. The container is now placed in a Soxhlet tube, in which it should be fitted somewhat loosely, and in which, in order to promote efficient drainage, two or three glass marbles have already been introduced. Extraction with pyridine is then commenced, the heat being so regulated that a brisk ebullition of the solvent takes place. The first extracts are coloured red, but usually, after the operation has proceeded for about half an hour, the liquid possesses merely the blue colour of pure indigotin. The digestion is then discontinued, and the Soxhlet tube holding the container drained as thoroughly as possible. The contents of the flask, which is preferably of the Erlenmeyer variety, are distilled down to a small bulk. The residual liquid is treated cautiously with boiling water (A), and again distilled, and this operation is repeated until the last traces of the pyridine have disappeared.\*

On cooling, the precipitate, which consists of a mixture of indirubin and indigotin in a crystalline condition, together with indigo-brown, is collected by means of asbestos in a Gooch crucible and washed with water. As a trace of the indigo-brown is present in combination with calcium or magnesium, and in this condition is insoluble in alkaline liquids, the mixed substances are first washed with hot 15 per cent. hydrochloric acid to remove this mineral matter, and then with hot 1 per cent. sodium hydroxide solution, which now completely dissolves the brown impurity. The product is finally treated with 1 per cent. acetic acid. The crucible and its contents are now placed in a small beaker, and, after drying, 5 c.c. of pure sulphuric acid are added. On heating the mixture for half an hour in a water-bath, sulphonation occurs, and the product is

that the latter, under the conditions of experiment, caused the formation of cupric hydrate. For instance, if a saturated pyridine solution of indigotin is digested at the boiling point with a little cupric hydrate, the colour of the solution is almost immediately discharged, and this effect was also observed to occur towards the end of the actual analytical process. It is probable that the oxidation product of the indigo which is thus formed is dehydroindigotin (*loc. cit.*).

\* The quantity of pyridine employed for the extraction is immaterial, and not dissimilar quantities as 400 c.c. and 75 c.c. have been found equally useful. The loss of solvent during each analysis has been approximately 15 c.c., and this could, so far as the results are concerned, be easily replaced. König's "pyridin puriss" is excellent for this purpose.

the residue in the water, the liquid filtered into a 200 c.c. flask and made up to this volume. The quantity of each colouring matter present in this solution as sulphonic acid is estimated by means of the Duboscq colorimeter, by comparison with standard mixtures of pure indigotin- and indiruhin-sulphonic acids prepared in a similar manner and containing 1 gram of the colouring matter per litre. As a general rule, the most satisfactory dilution for this purpose was found to be 5 c.c. of the standards, and also of the sample solution in 200 c.c. of water, but in the case of the isolation of mere traces of indiruhin a concentration of not less than 5 c.c. of the sample solution in 50 c.c. of water was then necessary.

In order to gauge the accuracy of the colorimetric determinations, the sample solution was also estimated as regards the total amount of colouring matter present by means of titanium chloride. For this purpose 25 c.c. of the solution were employed, together with 10 c.c. of 20 per cent. sodium tartrate, the somewhat excessive quantity of this latter being necessary on account of the large proportion of mineral acid present. In other respects the operation was carried out according to the modification of Knecht's process (*J. Soc. Dyers*, 1903, 3, 66) employed by one of us in previous work (Bloxam, *J. Soc. Chem. Ind.*, 1906, 25, 735), except that the titration was performed in purified hydrogen in the place of carbon dioxide.

As will be observed in the subsequent tables, the colorimetric and titanium chloride figures agree closely with one another, and having thus established the accuracy of the former method it will not be necessary in the subsequent use of the process to employ the latter as an adjunct.

*The Residual Indigotin.*—The container, and its contents which had been extracted by the pyridine without removal from the Soxhlet apparatus, were washed by percolation with water, and in the event of these washings being coloured by means of the trace of the pyridine solution of indigotin which remained in the container, this water was employed at the stage (A) (p. 1466) of the process. Subsequently the residue was repeatedly percolated with boiling 10 per cent. sulphuric acid, which effects the removal of the indigo gluten together with some of the mineral matter, and finally with boiling water until free from acid.

The cloth is now removed from the container, and by gently pushing the upper asbestos layer with a stout glass rod the contents of the tube are transferred to a spouted beaker of about 100 c.c. capacity, an operation which is readily performed without an adherence of any colouring matter to the sides of the tube. The whole is now dried in the water-oven, and after an addition of

10 c.c. of pure sulphuric acid, the colouring matter present is sulphated in the usual way.

The product diluted with water is filtered into a liter flask, finally made up with water to that volume, and an aliquot portion titrated with potassium permanganate, according to the directions previously given (Bloxam, *loc. cit.*), and in which 1 c.c. of the reagent is equivalent to 0.00222 gram of indigotin.

In order to test the accuracy of the process, known mixtures of the pure colouring matters were at first employed, and the following table illustrates the results obtained:

Composition of mixture	Total colouring matter	Total colouring matter, by	Values	Values
	Blue by $\text{KMnO}_4$ , red by $\text{TiCl}_3$	$\text{KMnO}_4$ , and colorimeter.	blue and red respectively by $\text{KMnO}_4$ and $\text{TiCl}_3$	blue and red respectively by $\text{KMnO}_4$ and colorimeter.
Blue 80.00 Red 20.00	100.32	99.79	Blue 79.27 Red 21.04	78.75 21.04
Blue 85.00 Red 15.00	100.17	100.03	Blue 85.20 Red 14.96	85.07 14.96
Blue 90.00 Red 10.00	100.08	100.51	Blue 90.66 Red 10.32	90.52 10.32
Blue 95.00 Red 5.00	100.69	99.51	Blue 95.68 Red 5.01	94.50 5.01
Blue 99.00 Red 1.00	99.96	99.66	Blue 98.82 Red 1.14	98.52 1.14

Having therefore ascertained that the method gave sufficiently accurate results, its application to natural indigos was now studied.

It is well known that Java indigo, as a rule, contains appreciable quantities of indirubin, and some varieties of this product, obtained through the kindness of Prof. van Romburgh, were available for examination. These samples were representative of three distinct processes: (a) the new process with hot water, (b) the new process with cold water, and (c) the old process, in which no chemicals are used. The exact manner in which indigo has been manufactured in Java has remained more or less of a secret, so that an examination of these authentic preparations was not devoid of interest.

During the analyses more than one titration of the sulphated colouring matter was carried out, and the maximum and minimum results are given in the tables.

*Java Indigo.—New Process with Hot Water.*

No. of sample	Total red and blue, maximum.	Total red and blue, minimum.	Total blue, maximum.	Total blue, minimum.	Red.
1	75.20	75.10	67.76	67.67	7.43
1	75.00	74.80	67.99	67.79	7.01
1	75.61	75.53	68.23	68.15	7.38
1	73.60	73.37	64.08	63.86	9.31
2	73.46	72.41	64.22	63.76	7.75
3	66.13	66.96	61.41	60.96	5.61
4	67.13	66.55	60.32	59.74	6.31
6	62.91	62.36	57.90	57.35	5.01

*Java Indigo.—New Process with Cold Water.*

7	72.88	72.29	69.82	69.23	3.06
7	72.82	—	69.50	—	3.32
8	71.02	70.39	66.98	66.35	4.04
9	68.30	67.76	56.15	55.61	2.15
10	71.90	71.46	69.86	69.42	2.04
11	61.71	61.48	59.21	58.98	2.50
12	62.71	62.21	59.18	58.68	3.53

*Java Indigo.—Old Process without Chemicals.*

13	75.28	—	71.80	73.08	1.48
13	75.28	—	71.88	72.71	1.40
13	75.27	75.06	73.88	73.67	1.39
13	74.96	74.63	73.22	72.89	1.74
14	73.10	72.72	71.93	71.55	1.17
14	73.10	72.73	71.88	71.51	1.22
15	69.54	69.25	68.41	68.15	1.10
15	69.54	69.25	68.80	68.26	0.99

*Analysis of Results.*

	Average value blue and red.	Average value total blue.	Average value red.
New process, hot water	71.62	64.59	7.07
" " cold	66.98	64.03	2.95
Old " without chemicals.	73.20	71.90	1.30

So far so interesting in connexion with the examination of these Java Indigo samples is the statement of Koppeschaar in the paper previously referred to, that van Lookeren Campagne has the credit of finding a method of preparing indigo from the Natal plant (*I. erecta*) in Java which gives twice or thrice the yield. On the other hand, he further remarks that the whole character of the indigo is changed, the percentage of red being much greater than usual, sometimes exceeding 10 per cent. The process here referred to by Koppeschaar, in the light of the above results, would appear to be identical with "the new process with hot water."

It is well known that hot water processes of indigo manufacture

...favoured by the Dutch ...  
 ...to connect the excessive quantity of indirubin which so  
 ...occurs in the Java variety, with the presence of tem-  
 ...The air-oxidation of indoxyl solutions in the presence of  
 ...of alkali or ammonia tends in a similar direction, but it  
 ...have shown (*Trans. loc. cit.*) that in these circumstances a  
 ...in the yield of colouring matter thus occurs, a point which  
 ...not likely to have escaped the observation of the Dutch chemist.  
 ...was noted during the laboratory experiments on the formation  
 ...indigo from pure indican (*loc. cit.*) that the dyestuff thus pro-  
 ...dured contained somewhat more indirubin than is usually present  
 ...most of the Indian commercial samples previously examined  
 (*loc. cit.*), and the only reasonable method for accounting for this  
 discrepancy is the fact that the temperature of the liquid during  
 air oxidation was maintained steadily at 60°. It is to be remem-  
 bered that this indirubin formation probably occurs at the earlier  
 stage of the oxidation, because the presence of free indoxyl is  
 necessary in order that the reaction with the isatin may take place.  
 On the other hand, with the Indian factory process, the average  
 temperature of the oxidation will be lower, although by the effect  
 of the steam blowers it will ultimately reach this point. Again,  
 Rawson (*Report on the Cultivation and Manufacture of Indigo*,  
*Manikgopore, 1904*) states that after a hot water fermentation the  
 liquid must at once be submitted to oxidation to avoid a subsequent  
 loss of colouring matter, and it would therefore appear to follow  
 that in such a process the temperature during the latter operation  
 is necessarily higher than that in vogue by the ordinary method.  
 It seems likely therefore that the high percentage of red in the  
 new process with hot water samples of Java indigo arises from the  
 fact that during their manufacture the oxidation of indoxyl in  
 the presence of a trace of alkali or ammonia has been carried out  
 at a higher temperature than usual.

Among the Indian varieties of natural indigo, that produced in  
 the past by the "Coventry Lime and Acid process" has been  
 noted as containing some quantity of indirubin. It is referred  
 to by Koppeschaar, who states that Coventry's method is used  
 in British India, and that the indigo prepared by this method  
 contains much indigo-red, but less indigotin than good samples  
 of Java indigo (*loc. cit.*). A description of the process has  
 been given in a previous paper (*loc. cit.*), and the indigo which  
 is there produced arises from the air-oxidation of indoxyl in the  
 presence of lime-water. An authentic sample of this indigo  
 has been preserved in the Dyeing Department of the Leeds  
 University and was available for examination by the pyridine

and the results are given in the following table:

#### Coventry Process Indigo.

Total red and blue, maximum.	Total red and blue, minimum.	Total blue, maximum.	Total blue, minimum.	Red.
61.76	61.44	56.53	56.21	5.23
61.76	60.77	56.73	55.74	6.02
61.20	60.97	56.50	56.27	4.70
61.23	61.19	56.40	56.21	4.96

Finally, an analysis is given of two samples of indigo prepared in the laboratory, the first of which is curious on account of the large amount of indirubin which it contains. This product (A) was obtained by the hydrolysis of indican (0.9996 gram) with 2 grams of the enzyme for five hours and a half at 50–52° in the presence of 3.7 c.c. of  $N/10$  sulphuric acid, and the operation was carried out in the absence of air and in the manner described fully in a previous communication (*loc. cit.*). The indoxyl solution was then oxidized with air at 60° after the addition of 18.5 c.c. of  $N/2$  ammonia, and apparently the whole operation was conducted in the usual manner. The result, however, is quite abnormal, and is merely referred to as showing the possibility of the formation of very large quantities of indirubin during the oxidation process. The second sample (B) represents the product of the hydrolysis of indican by acid and simultaneous oxidation with air, and in which 0.5 gram of indican in 850 c.c. of water at 60° was treated with 15 c.c. of 33 per cent. hydrochloric acid, and air aspirated through the solution for eight hours.

Total red and blue, maximum.	Total red and blue, minimum.	Total blue, maximum.	Total blue, minimum.	Red.
88.90	88.13	63.07	62.39	25.73
93.5	—	—	—	1.54

#### Estimation of Indigo Brown.

A point of interest in this pyridine process for the analysis of indigo containing indirubin is that it is also possible to estimate approximately at the same time the amount of indigo-brown which is present in the sample. It has been previously shown that this mixture of brown substances can be removed from the dyestuff by means of pyridine (Trans., 1907, 91, 279), and consequently in this analytical method it is contained, or mostly so, in the crude indirubin precipitate which remains after the removal of the solvent. On the other hand, it was ascertained that the aqueous filtrate (A) from this precipitate contains a small quantity of one of the more soluble



same constituents. In carrying out therefore the new process, the indigo precipitate is washed with hot dilute sodium hydroxide solution, the dark brown extract neutralized with acid, and when all the deposited indigo-brown is collected and weighed, the filtrate being reserved. The filtrates A and B are then extracted with one other, the solution washed with water, and then evaporated, and the weight of this residue added to that of the main bulk. A defect in the method of indigo-brown analysis is the occasional presence in samples of Java indigo and other indigos prepared from the *I. arrecta* of indigo-yellow or kempferol (Trans., 1907, 91, 435), because this substance is soluble in pyridine and in alkaline solutions, and is reprecipitated from the latter by means of acid. A search for this product in the samples under examination indicated that in the case of the Java varieties it was present to the extent of not more than 0.2 per cent., and would thus not materially affect the results, that it was absent in the case of the Coventry indigo, and that merely a trace was present in the new product from Bengal. As is well known, the Indian manufacturers are now employing the Java or Natal plant (*I. arrecta*) in place of the *sumatrana*, and the Bengal sample referred to above, and which was kindly procured for us by Mr. Oliver Marsden, of Leeds, was shown to have been prepared from the first-named plant. An analysis carried out by the tetrasulphonate process indicated 68.3 of coloring matter.

#### Indigo-Brown in various Indigos (air dried).

Java indigo, new process, hot water.	Java indigo, new process, cold water.	Java indigo, ordinary process.	Coventry process, indigo.	New Bengal indigo.
5.4	5.2	11.5	8.7	9.50

It is therefore evident that Java indigos contain approximately one-half the indigo-brown which is present in the newest Indian variety, and a point which can only arise from details of manufacture. In an earlier investigation (Trans., 1907, 91, 279), the amount of crude pyridine extract obtained from a mixture of numerous samples of Bengal indigo which had been prepared from the *I. sumatrana* worked out to 14 per cent., and although this mixture of samples without doubt contained considerably more indigo-brown than that contained in the new Bengal product just referred to, this value is somewhat too high for direct comparison. It also includes, as was demonstrated at the time, some quantity of mineral matter. There is the strongest reason to regard indigo-brown as a waste product of the manufacture, and this has recently

received considerable support from the isolation of a closely similar, if not identical, compound from the mixture of substances produced by the decomposition of indoxyllic acid (Trans., 1909, 93, 847).

It has been pointed out by one of us (Bloxam, *loc. cit.*) that when Bengal indigo has been freed from indigo gluten by means of dilute sulphuric acid, and the residue is then extracted with pyridine, it is only possible in this way to prepare an indigotin of about 91 per cent. purity. That this arose to some extent from obstinately retained mineral matter and plant debris was evident, but, on the other hand, the deficiency could not be entirely accounted for in this way. Further experiment now indicates that most indigos contain a small percentage of a brown impurity, insoluble in pyridine, and apparently in all solvents, but which dissolves to some extent in alkali to form a blackish-brown solution. On sulphonating, for instance, an indigo which has been purified by means of acid and pyridine with ordinary sulphuric acid, or, indeed, any commercial indigo, this compound is not attacked, and when the product is diluted with water it is precipitated apparently unchanged. In the analytical method described by Rawson (*J. Soc. Chem. Ind.*, 1899, 18, 251), this brown material, at least in part, consists of the impurity which is carried down by a precipitation of barium sulphate in the liquid. As no data are available, it is useless to speculate as to the origin of this product, although its general characteristics suggest that it is allied to indigo-brown.

#### *The Analysis of Indigo by the Pyridine Method.*

For the accurate estimate of ordinary indigo it is now well recognised that it is necessary to eliminate the impurities which accompany the colouring matter, previous to or after the sulphonation process, and before the actual titration, because the sulphonation products of indigo-brown, and to a special degree those of indigo gluten, readily reduce the permanganate. These difficulties are avoided by the employment of the "tetrasulphonate" process, a full description of which is given by one of us elsewhere (Bloxam, *loc. cit.*). There could apparently be no doubt that by adopting the pyridine extraction method of analysis as above described, and by which a gradual elimination of the impurities is effected, an accurate estimation of indigo apart from the question of indirubin could be carried out, and the point was interesting as involving a further test of the trustworthiness of the tetrasulphonate process.

For the purpose of experiment a sample of Bengal indigo, containing but a trace of indirubin, was employed, and the procedure was exactly similar to that given above. For the analysis both

pyridine and the tetrasulphonate method, and the results were carried out in each case with potassium permanganate and sodium chloride:

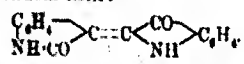
Pyridine method .....	{ $\text{KMnO}_4$ = 66.27 per cent.	Mean = 66.27
	{ $\text{TKI}_2$ = 66.13 "	
Tetrasulphonate method .....	{ $\text{KMnO}_4$ = 66.49 per cent.	Mean = 66.47
	{ $\text{TKI}_2$ = 66.46 "	

The results given by the two methods thus harmonise remarkably and this was to be anticipated on account of the numerous proofs which have been previously given by one of us (*loc. cit.*) as to the accuracy of the tetrasulphonate method.

Finally, it will no doubt be quite possible to analyse indigo with fair accuracy according to the pyridine method, by means of the Duboscq tintometer alone, but the employment of this process for practical purposes, with regard to indigo more or less free from indirubin, is not suggested on account of the somewhat lengthy operations involved.

### The Effect of Indirubin in the Dyeing Operation.

In regard to the advantage or otherwise of the presence of indirubin in indigo, there has been considerable difference of opinion, and this still exists to some extent among dyers at the present time. According to Rawson and Knecht (*J. Soc. Dyers*, 1888, 4), and also to Hummel (*ibid.*), indirubin is a valuable dyestuff, and is extremely fast to light. Matthews (*J. Soc. Chem. Ind.*, 1902, 21, 222), however, points out that, in addition to other disadvantages, indirubin requires for reduction a much stronger reagent than indigotin, and that as a result the greater part of this dyestuff is not attacked in the indigo vat, but settles down to the bottom of the receptacle. Fasal (*Mitt. K. Tech. Gew.-Mus. Wien.*, 1895, 11, 307) found that the shade of colour given by an indirubin vat became bluer from day to day, and that ultimately a pure indigo blue was produced. This change of tinctorial property was shown by this author to be due to the further reduction of leucoindirubin with the formation of indoxyl, and that this was oxidised on the fabric to indigotin. A more recent investigation of the reaction by one of us (*Proc.*, 1909, 25, 177) indicates that, in addition to indoxyl, oxindol is simultaneously produced, and that this should be the case is readily understood from the formula of indirubin itself:



It therefore is evident that indirubin possesses little value as a dyestuff, and its presence in indigo cannot be considered of

indirubin, which is probably produced not more than in small quantities.

On the other hand, indirubinindisulphonic acid is according to Paul (1907) and also to Rawson and Knecht (*loc. cit.*), a weakly coloured and gives colours much faster to light than the corresponding indigo extract, which is sodium indigotinindisulphonate.

The statement of Bergtheil (*Report of the Indigo Research Station, Stralab, 1906*), "Preliminary examination . . . has shown decisively that there is more than one red body in most commercial indigos," cannot be correct, because in all indigos at present experimented with in this and other investigations, no red substance other than indirubin has been detected.

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## XXXVI.—The Relative Influence of the Ketonic and Ethenoid Linkings on Refractive Power.

By IDA SMEDLEY.

THE exaltation in refractive power produced by the conjugation of unsaturated radicles, both with the carbonyl and with groups containing an ethenoid linking, has been discussed by several observers (Gladstone, *Proc. Roy. Soc.*, 1881, 31, 327; Brühl, *Ber.*, 1907, 40, 893; Perkin, *Trans.*, 1907, 91, 806; Smedley, *Trans.*, 1908, 93, 372; 1909, 95, 218); it seemed possible, however, that the results already obtained might be somewhat simplified by making a quantitative comparison of the effect produced on the refractive power by the ketonic\* and ethenoid linkings respectively under various conditions of conjugation.

If the exaltation of refractive power, produced by the mutual conjugation of groups containing the ethenoid linking, were the same as that produced by the conjugation of such groups with the carbonyl radicle, there should be a constant difference between the molecular refractions of any two compounds containing respectively the groups  $C=CH_2$  and  $C=O$ , but otherwise similarly constituted.

It will be seen from the accompanying table that when placed at one end of a chain of conjugated unsaturated groups, the incre-

\* The phrase "ketonic linking" is used in this paper to represent the double linking in the group  $C=O$ , whether the latter is present in an aldehyde or ketone group.

1476. BRIDLEY: THE RELATIVE INFLUENCE OF THE CARBONYL GROUP IN REFRACTIVE POWER WHEN A  $>C=CH_2$  GROUP IS SUBSTITUTED BY A  $>C=O$  GROUP VARIES ONLY BETWEEN THE LIMITS 1.5 AND 1.7, ALTHOUGH THE NUMBER OF UNSATURATED GROUPS ENTERING INTO CONJUGATION CHANGES CONSIDERABLY.

Table showing Increments in Refractive Power on replacing  $C=O$  by  $C=CH_2$ .

Name	Formula	$M_A$	Increment	Observer
Formaldehyde	$H_2CO$	6.96	—	Estimated <sup>1</sup>
Ethylene	$H_2C=CH_2$	10.77	3.81	Living and Dewar
Acetone	$Me_2CO$	16.05	—	Brühl
isobutylene	$Me_2C=CH_2$	19.91	3.86	Estimated <sup>1</sup>
Ethylidenecetone	$CH_3CH=CHMe$	25.53	—	Estimated <sup>1</sup> ; f
Dimethylbutadiene	$CH_3CH=CHCH=CHMe$	30.38	4.85	Brühl
Maleic dialdehyde	$HOOCCH=CHCOOH$	21.08	—	Estimated <sup>1</sup>
Hexatriene	$CH_2=CHCH=CHCH=CH_2$	39.58	$9.5/2 = 4.75$	Parkes
Benzaldehyde	$PhCHO$	31.77	—	Brühl
Styrene	$PhCH=CH_2$	35.98	4.21	..
Benzophenone	$Ph_2CO$	56.20	—	Rykman
α-Diphenylethylene	$Ph_2C=CH_2$	60.10	3.90	..
Cinnamaldehyde	$PhCH=CHCHO$	43.51	—	Brühl
Phenylbutadiene	$PhCH=CHCH=CH_2$	48.00	4.49	Klages
Benzylidenacetone	$PhCH=CHMe$	48.54	—	See p. 1482
Phenylmethylbutadiene	$PhCH_2CH=CHCH=CH_2$	52.61	4.07	Klages
M. Acetaldehyde	$CH_3CHO$	11.50	M. Mesityl oxide	30.17
$CH_2$ in aldehyde series		4.54	$CH_2$ in ketone series	4.07
M. Formaldehyde		6.96	M. Ethylidenecetone	35.56
M. Ethylene		10.77	M. Maleic acid	23.94
$2 \times CH_2$ increment		9.14	$2(MeCO_2H - MeCHO)$	2.36
M. isobutylene		19.91	M. Maleic dialdehyde	21.08

<sup>1</sup> The molecular refraction for the sodium line is found to be 25.76 (Auer and Henschler, *Ber.*, 1910, 43, 917).

If now a comparison is made of the refraction increments obtained on substituting an ethenoid for a ketonic linking when it occurs, not at the end of a series of unsaturated hydrocarbon radicals, but in the middle of such a chain, much greater differences are observed.

Compound	Formula	M.	Increment	Observer
Benzophenone	$\text{Ph} \cdot \text{C}(=\text{O}) \cdot \text{Ph}$	55.95	—	Calkins
Diphenylmethane	$\text{Ph} \cdot \text{CH}_2 \cdot \text{Ph}$	54.20	0.45	Kytnann
Diphenylbutadiene	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{Ph}$	52.9	—	Smedley
Benzylidenacetophenone	$\text{Ph} \cdot \text{CH}=\text{O}$	70.55	11.35	P. 1453
Diphenylbutatriene	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH} \equiv \text{CH} \cdot \text{Ph}$	106.9	—	Smedley
Cinnamylidenacetophenone	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{O}$	87.6	13.3	P. 1453
Dibenzylidenacetone	$\text{Ph} \cdot \text{CH}=\text{O}$	84.0	14.9	P. 1453

When a carbonyl group is interposed in a chain of contiguous ethenoid groups, the exaltation of the refractive power is so much diminished that the increase in the molecular refraction of the compound produced by the addition of the carbonyl group may fall to 1 unit, as shown in the following table, a value much below that assigned to the same group in saturated aliphatic compounds (4.7 units). This may perhaps be regarded as evidence in favour of the view that in a chain of contiguous ethenoid linkings the effect of each unsaturated group is not confined to the adjacent groups, but is transmitted along the whole chain, increasing the refractive effect of each link (compare Smedley, Trans., 1908, 93, 372).

Table showing the Effect on Refractive Power of introducing a Carbonyl Group into Aromatic Hydrocarbons.

(Refraction value of CO in fatty compounds = 4.70.)

Compound	Formula	M.	Increment
Benzophenone	$\text{Ph} \cdot \text{C}(=\text{O}) \cdot \text{Ph}$	56.20	—
Diphenyl	$\text{Ph} \cdot \text{Ph}$	51.93	4.27
Benzylidenacetophenone	$\text{Ph} \cdot \text{CH}=\text{O}$	70.55	—
Stilbene	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{Ph}$	65.65	4.9
Cinnamylidenacetophenone	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{O}$	87.6	—
Diphenylbutadiene	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{CH} \cdot \text{Ph}$	82.9	4.7
Dibenzylidenacetone	$\text{Ph} \cdot \text{CH}=\text{O}$	84.0	—
Diphenylbutatriene	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH} \equiv \text{CH} \cdot \text{Ph}$	82.9	1.1
Cinnamylidenbenzylidenacetone	$\text{Ph} \cdot \text{CH}=\text{CH} \cdot \text{CH}=\text{O}$	102.7	—

## Refraction value of CO in fatty compounds

Diphenylketone	$\text{Ph}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{Ph}$	50.7	1.6
Acetophenone	$\text{Ph}-\text{CO}-\text{Me}$	50.30	—
Toluene	$\text{Ph}-\text{Me}$	50.30	5.2
Benzaldehyde	$\text{Ph}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}$	48.51	—
Styrene	$\text{Ph}-\text{CH}=\text{CH}_2$	35.90	7.3
Cinnamylideneacetone	$\text{Ph}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CO}-\text{Me}$	64.3	—
Phenylmethylketone	$\text{Ph}-\text{CH}_2-\text{CO}-\text{Me}$	52.6	11.6

A comparison of the two isomeric diphenylethylenes with benzophenone suggests that the effect of the ketonic linking still resembles that of the ethenoid linking, but when interposed between two unsaturated radicals, the ketonic must be compared with an ethenoid linking which itself joins a side-chain:

	$M_s$		$M_s$
Baillone, $\text{Ph}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{CH}-\text{Ph}$	65.65	Diphenylethylene, $\text{Ph}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}=\text{CH}-\text{Ph}$	69.16
Benzophenone, $\text{Ph}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{Ph}$	56.23	Benzophenone, $\text{Ph}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{Ph}$	56.26
	5.15		3.9

The difference in the refractive power of the isomeric cinnamylideneacetone and dibenzylideneacetone is well marked; the molecular refraction of the compound containing the longer chain of conjugated unsaturated linkings exceeds by 3.6 units the refraction value of the symmetrically arranged isomeride.

Since writing the above, my attention has been called to a paper published by Auwers and Eisenlohr (*Ber.*, 1910, **43**, 806), in which the effect of the conjugation of unsaturated groups is discussed. These authors quote the statement of Bruhl (*Ber.*, 1907, **40**, 1153)

that the group  $\text{C}(\text{O})_2$  does not produce exaltation of refraction;

the present author has previously pointed out that in aromatic compounds this group produces a marked effect on refraction (compare Armstrong and Robertson, *Trans.*, 1905, **87**, 1275; Smedley, 1909, **95**, 221), and has suggested that the peculiar influence of this group is to be attributed rather to the mutual influence of the oxygen atoms.

Auwers and Eisenlohr draw the conclusion that the substitution of an alkoxy-group for a hydrogen atom decreases the exaltation of refractive power produced by conjugation, and contend further

that a small amount of error is produced by substituting an alkyl group for an alkyl or hydroxy group. There appears to be an error in the figure quoted for the molecular refraction of crotonaldehyde. The value for the sodium line calculated from Brühl's data, to which reference is made, is 44.14 instead of 45.21, a difference which removes one instance of the three quoted. There is also always possibility of error when values are calculated from the atomic refractions, and when, for instance, the value for the carbonyl group is assumed to be identical in aldehydes and ketones; instead of using the method adopted by Auwers, the following basis of comparison may be employed, which is independent of calculated values for the atomic refractions.

	M. R.	Difference, R <sup>COOM</sup> - R <sup>COH</sup>		M. R.	Difference, R <sup>COOM</sup> - R <sup>COH</sup>
Acetone	16.13		Acetic acid	12.99	
Acetaldehyde	11.56	4.57	Acetaldehyde	11.56	
			Butyric acid	22.16	1.48
			Butaldehyde	20.62	
Ethylbenzeneacetone	25.78		Crotonic acid *	22.63	1.54
Crotonaldehyde	21.47	4.31	Crotonaldehyde	21.47	
Acetophenone	36.34				1.16
Benzaldehyde	32.02	4.32			
Benzylbenzeneacetone	48.41				
Cinnamaldehyde	44.14	4.27			

\* Auwers and Eisenlohr (*Ber.*, 1910, 43, -17). The value given for crotonic acid is for the α-line.

	M. R.	Difference, R <sup>COOM</sup> - R <sup>COH</sup>		M. R.	Difference, R <sup>COOM</sup> - R <sup>COH</sup>
Methyl acetate	18.11		Ethyl acetate	22.24	
Acetaldehyde	11.56	6.55	Acetaldehyde	11.56	
					10.68
Methyl butyrate	20.91		Ethyl butyrate	31.25	
Butaldehyde	20.62	6.29	Butaldehyde	20.62	
					10.78
			Ethyl crotonate	31.68	
			Crotonaldehyde	21.47	
					10.21
Ethylbenzoate	37.80		Ethylbenzoate	42.56	
Benzaldehyde	32.02	5.78	Benzaldehyde	32.02	
					10.53
Methyl cinnamate	49.31		Ethyl cinnamate	64.19	
Cinnamaldehyde	44.14	5.17	Cinnamaldehyde	44.14	
					10.05

A study of the above table shows that the difference in molecular refraction between an aldehyde and the corresponding methyl ketone varies very slightly in saturated and unsaturated com-



pounds. The distinction which takes place in this direction in the unsaturated compounds quoted is so slight that but little importance can be attached to it. The distinction drawn by Auwers and Eisenlohr between the influence of the hydroxyl and that of the alkyl group does not appear to be warranted by the evidence given. The difference between the molecular refractions of crotonic acid and aldehyde is slightly lower than the corresponding difference in the aliphatic series; similarly, there is a decrease in the increment of the molecular refraction of crotonic ester over that of crotonaldehyde. This diminution is intensified in the cinnamic series, but the value for cinnamic acid, which has only been examined in solution, is excluded from the table; and the numbers for the crotonic series alone do not appear to warrant any distinction being made between the behaviour of the acid and its esters.

It is probable that the diminished effect produced by the conjugation of the carbonyl group in acids and esters, as compared with that in ketones and aldehydes, may be attributed to the mutual effect of the two oxygen atoms whereby the residual affinity of the carbonyl oxygen is lessened (Trans., 1909, 95, 231).

Auwers and Eisenlohr also discuss the question of "crossed double bonds," and are led to the conclusion that if three "crossed double bonds" are present, the exaltation of refractive power is much slighter than when three conjugated double bonds are present in an open chain, and remains below that of the related substances containing only two conjugated double bonds. The present author's results show that when the number of unsaturated groups is considerably increased, the two side-chains terminating in the same unsaturated group do have marked effect on each other in exalting refractive power.

Substance	(Observed) $M_d$	Calculated Value	Difference
Benzophenone, O Ph-C(=O)-Ph		$M_d$ Ph-C(=O)Me 36.00 Ph-C(=O)Me 36.00 — 72.00 $- M_d$ COMe, 16.05 — 55.95	
	56.20	55.95	+0.25
Benzylideneacetophenone, HHC(=O)Ph Ph-C(=O)-CH=CH-Ph		HH $M_d$ Ph-C(=O)C(=O)Me 48.54 Ph-C(=O)Me 36.00 — 84.54 $- M_d$ COMe, 16.05 — 68.49	
	70.55	68.49	+2.1

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Substance	(Observed) M <sub>d</sub>	Calculated Value	Difference
<b>Isobutylenesulphonate</b> HNOHH Ph-C(=O)-C(=O)-Ph		HH M <sub>d</sub> Ph-C(=O)-C(=O)-Ph 48.54 HH Ph-C(=O)-C(=O)-Ph 48.54 97.08 - M <sub>d</sub> COM <sub>2</sub> 16.05 81.03	3.0
	84.00		
<b>Cinnamylidenesulphonate</b> HHHHO Ph-C(=O)-C(=O)-Ph		HHHH M <sub>d</sub> Ph-C(=O)-C(=O)-COM <sub>2</sub> 64.19 Ph-C(=O)-COM <sub>2</sub> 36.00 100.19 - M <sub>d</sub> COM <sub>2</sub> 16.05 84.14	3.45
	87.59		
<b>Cinnamylidenesulphonate</b> HHHHHH Ph-C(=O)-C(=O)-C(=O)-Ph		HHHH M <sub>d</sub> Ph-C(=O)-C(=O)-COM <sub>2</sub> 64.19 HH Ph-C(=O)-COM <sub>2</sub> 48.54 112.73 - M <sub>d</sub> COM <sub>2</sub> 16.05 96.68	6.0
	102.7		
<b>Diacinnamylidenesulphonate</b> HHHHHHHH Ph-C(=O)-C(=O)-C(=O)-C(=O)-Ph		HHHH M <sub>d</sub> Ph-C(=O)-C(=O)-COM <sub>2</sub> 64.19 HHHH Ph-C(=O)-C(=O)-COM <sub>2</sub> 64.19 128.38 - M <sub>d</sub> COM <sub>2</sub> 16.05 112.33	9.2
	121.5		

In the accompanying table, a method of calculation is used in which the exaltation effect of each side chain of groups containing ethenoid linkings with the contiguous carbonyl radicle is separately allowed for and the minimum value of one carbonyl group subtracted. If the two side-chains of groups containing ethenoid linkings have no effect on each other through the carbonyl radicle, the values calculated should be higher than that actually observed, since the minimum value for a carbonyl group has been subtracted. Yet as the number of groups conjugated is increased in each chain, the observed value becomes markedly greater than that calculated; in some manner therefore the two chains of unsaturated radicles present on either side of, and each terminating in, the same carbonyl group are able to influence each other. It is a point of some interest whether the  $>CH_2$  group acts similarly

to the  $>\text{CO}$  group, or whether it is only when associated with an unsaturated group that this imperfect screening effect is present. At present sufficient data are not available to enable this point to be decided with certainty. It may be that the exaltation of refractive power is caused by the conjugation of the chain of groups containing ethanoid linkings with a carbonyl group, the influence of which has already been exalted by the second chain of unsaturated groups to which it is contiguous, or it may be that the screening effect is not connected with the unsaturated character of the group interposed. The determinations of magnetic rotation by Perkin (Trans., 1896, 69, 1691) to the conclusion that the screening effect of the carbonyl is greater than that of the methylene group. There are, however, considerable differences in the relative influence of the  $\text{CO}$  and  $\text{CH}_2$  groups on rotation and refraction. The association of carbonyl with the phenyl nucleus has a reducing influence on the rotation value of the phenyl group—a result which appears to be entirely at variance with the exaltation of refractive power produced by the conjugation of the same groups; the molecular refraction of benzaldehyde is greater than that of toluene, but the magnetic rotation of the former is less.

#### EXPERIMENTAL

##### Determinations of Refractive Power

(1) *Benzylidenacetone* in chloroform solution. This substance was obtained from Kahlebaum and was recrystallised from alcohol. Melting point  $41-42^\circ$ .

Percentage strength of solution.	$M_D$	$M_A$	$M_p$
9.6273	48.75	51.69	53.65
8.1535	48.27	51.06	53.80
6.8712	48.56	51.33	54.07
11.6295	48.79	51.92	53.63
Mean	48.52*	51.31	53.79

$$M_D - M_A = 2.81; M_p - M_A = 5.27$$

\* Answers and Knebelohr (Ber., 1910, 43, 817) find, for the pure substance,  $M_D = 45.41$ .

(2) *Benzylidenacetophenone* in chloroform solution. Melting point  $58^\circ$ .

Percentage strength of solution.	$M_D$	$M_A$	$M_p$
8.6935	70.60	75.49	80.36
4.6774	70.42	75.12	81.04
10.5830	70.43	75.30	79.33
Mean	70.48	75.27	80.25

$$M_D - M_A = 4.79; M_p - M_A = 9.77.$$

(3) *Cinnamylidenacetone* (Diels, *Ber.*, 1885, 18, 2331) in chloroform solution. Melting point 68--69°. The product must be recrystallized before using, as it decomposes on keeping, forming an oily residue containing both acetic acid and cinnamaldehyde:

Percentage strength of solution.	$M_D$	$M_A$
8.0070	64.24	70.92
8.8710	64.27	70.79
9.4874	63.96	70.65
3.4855	64.24	71.07
6.8150	64.54	
11.8473	65.27	70.88
Mean	64.19	70.76

$$M_D - M_A = 6.57.$$

(4) *Dibenzylidenacetone* in chloroform solution. The specimen used was obtained from Kahlbaum, when crystallized from alcohol it melted at 111--112°:

Percentage strength of solution.	$M_D$	$M_A$
12.0201	83.71	91.68
12.8012	83.81	91.70
11.8836	84.29	92.21
4.1027	84.06	93.08
Mean	84.04	92.17

$$M_D - M_A = 8.13$$

(5) *Cinnamylidenacetophenone* (Scholtz, *Ber.*, 1895, 28, 1730) in chloroform solution. Melting point 102°:

Percentage strength of solution.	$M_D$	$M_A$
5.7293	87.53	98.53
5.7298	87.25	98.10
17.4681	87.72	
5.2641	87.85	97.87
Mean	87.59	98.17

$$M_D - M_A = 10.58.$$

(6) *Cinnamylidenbenzylidenacetone* in chloroform solution. This substance, previously prepared by condensing cinnamylidenacetone with benzaldehyde (Scholtz, *Ber.*, 1895, 29, 614), was obtained as follows. 6.6 Grams of cinnamaldehyde and 7.3 grams of benzylidenacetone were dissolved in 150 grams of ethyl alcohol, and 200 c.c. of water and 20 grams of 10 per cent. aqueous sodium hydroxide were added. After a few minutes the milky solution became intensely yellow, and an oil separated, which, after twenty-four hours, solidified to a mass of yellow crystals. These, when

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recrystallized from a mixture of chloroform and alcohol, melted at  $109^{\circ}$ .

Percentage strength of solution	$M_d$
5.1341	102.69

(7) *Dicinnamylidenacetone* (Diedt, *Ber.*, 1885, 18, 2325) in chloroform solution. The yellow needles were recrystallized from acetone, and melted at  $142^{\circ}$ :

Percentage strength of solution	$M_d$
6.4411	121.79
2.7677	121.45
2.2599	122.16
7.1955	129.23

Much of the expense of this research has been met by a grant from the Research Fund Committee of the Chemical Society.

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## CXXXVII.—The Constitution of the $\beta$ -Diketones.

By ION SNEDELY

THE investigation both of the magnetic rotation and of the molecular refraction of ethyl acetoacetate and its alkyl derivatives by Perkin (*Trans.*, 1892, 61, 500) and Brühl (*Ber.*, 1892, 25, 369; *J. pr. Chem.*, 1891, [ii], 50, 131) led to the conclusion that these compounds were ketonic in structure. The study of the aliphatic  $\beta$ -diketones by the same observers showed that their physical constants did not accord with a diketonic structure. To acetylacetone a dienoic structure was ascribed (Brühl, *J. pr. Chem.*, 1894, [ii], 50, 192), the methyl derivative was regarded as keto-enolic, and the ethyl derivative as a true diketone.

In the light of our present knowledge as to the influence of the conjugation of unsaturated groups on the physical constants of compounds, it becomes necessary to revise the conclusions previously drawn as to the structure of the aliphatic  $\beta$ -diketones.

If the increment in refraction produced by the conjugation of an ethenoid with a carbonyl group be introduced, the calculated value for the molecular refraction of acetylacetone in its keto-enolic form agrees well with that observed. The particular type of conjugation occurring in the keto-enolic form of acetylacetone is found in ethyl crotonate, the refraction of which has been measured (Brühl, *loc. cit.*), and may therefore serve as a standard:

	M.R. <sub>a</sub> observed
Ethyl crotonate, $\text{H H O}$ $\text{Me} \cdot \text{C} \cdot \text{C} \cdot \text{C} \cdot \text{OEt}$ .....	31.5
The difference between the refraction values of corresponding ethyl and methyl esters varies from .....	4.5 to 4.1
Difference .....	27.0 to 27.4

The value for methyl crotonate may therefore be assumed to lie between 27.0 and 27.4. The molecular refractions of methyl crotonate (I) and the keto-enolic form of acetylacetone (II) should



closely resemble each other; the value actually observed for acetylacetone is 27.3 (Perkin) or 27.4 (Brühl). The evidence from refractive power accords therefore with the keto-enolic structure for acetylacetone, and it is unnecessary to assume the existence of the di-enolic form.

The substitution of a methyl group for one of the hydrogen atoms in acetylacetone is accompanied by an increase of 3.35 units in the observed molecular refraction (Perkin, *loc. cit.*):

$$\text{M.R.} = \left( \frac{M(n_d^2 - 1)}{d(n_d^2 + 2)} \right)$$

Methylacetylacetone	30.64
Acetylacetone	27.29
	3.35

A similar substitution in a compound where no change of constitution is probable is accompanied by an increase of approximately 4.5 units; the abnormally small increment in refraction which is observed when the methyl group is introduced into acetylacetone makes it appear probable that there is a difference of structure between acetylacetone and its methyl derivative.

The value actually observed for methylacetylacetone is intermediate between those required for the diketonic and keto-enolic forms respectively:

	M.R. <sub>a</sub>
Value estimated for the keto-enolic form (observed value for ethyl crotonate) .....	31.5
Value estimated for the diketonic form:	
M.R. <sub>a</sub> methyl ethyl ketone .....	29.57
M.R. <sub>a</sub> acetone .....	16.65
.....	36.6
Less M.R. <sub>a</sub> methane .....	6.6
.....	30.0
Value observed for methylacetylacetone .....	30.75

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A study of the magnetic rotatory power of the ethyl derivatives of acetylacetone led Perkin to the conclusion that the ethyl compound was a diketone, and the methyl derivative was intermediate between ethylacetylacetone and the unalkylated compound. Alkylation tended to produce the ketonic form. The same rule appears to apply to the refractive power.

The order of the increment caused by the conjugation of unsaturated groups becomes so much magnified in aromatic substances that deductions as to constitution may more safely be drawn, and it was therefore a matter of some interest to investigate the refractive power of the aromatic  $\beta$ -diketones.

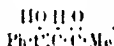
## Benzoylacetone.

The magnetic rotation of this compound was determined by Perkin, who found that it approached most nearly to that required by the hydroxy ketonic formula, being 1.051 units in excess of that calculated:

### Magnetic Rotation.

Calculated for hydroxy ketonic formula	17.731
Observed	19.782

In his investigation of the magnetic rotation of cinnamyl compounds, Perkin (Trans., 1896, 69, 1145) showed that all gave values higher than those calculated. The increments show some variation: in the case of benzylidenacetone it reaches 1.489 (4.333—2.834), whilst for cinnamaldehyde it is 0.89 (3.724—2.834). The increment observed in the case of benzoylacetone agrees therefore with its representation by the formula



The molecular refraction now determined in chloroform solution is

$$M_d = 50.3; M_y - M_x = 5.8.$$

A comparison of this value with that obtained for benzylidenacetone (this vol., p. 1482) shows that the observed value for benzoylacetone is in accordance with that required for a hydroxy derivative of benzylidenacetone:

	$M.R._d$	$M_y - M_x$
Benzylidenacetone	48.5	5.3
Replacement of H by OH	1.5	—
HO HO	—	—
Ph·C=C·C·Me	50.0	5.3
Observed for benzoylacetone	50.3	5.8

These results are within the limits of accuracy of the experimental method used.

*Dibenzoylmethane.*

The constitution of this substance was discussed by Wislicenus (Advan., 1899, 308, 219), who claimed to have isolated a diketonic form isomeric with the substance originally obtained by Baeyer and Perkin (*Ber.*, 1893, 16, 2134), to which latter Wislicenus therefore ascribed a hydroxy-ketonic structure. Subsequently, Ruhemann and Watson (*Trans.*, 1904, 85, 456) showed that the compound described by Wislicenus was not isomeric with dibenzoylmethane, but was the ethoxy-derivative of benzylidenacetophenone.

Dibenzoylmethane, obtained by the condensation of ethyl benzoate and acetophenone, is generally pink or red in colour (possibly due to the presence of traces of an iron salt), and it is difficult completely to remove this colour by recrystallisation. If, however, the dibenzoylmethane is dissolved in cold concentrated sulphuric acid and reprecipitated by water, its melting point is unchanged (78°), but it is now pale yellow in colour, nor is this colour removed by repeated recrystallisation. The colour is interesting, because it closely resembles that of benzylidenacetophenone, whereas in the alkyl derivatives of dibenzoylmethane no yellow colour could be detected. The ethoxy-derivative of benzylidenacetophenone appeared also to be persistently yellow. So far therefore as the argument from colour is concerned, benzylidenacetophenone, its ethoxy-derivative, and dibenzoylmethane may be classed together as pale yellow compounds. The alkyl derivatives of dibenzoylmethane are, however, colourless.

*Refractive Power.*—The values estimated for the hydroxy- and ethoxy-derivatives of benzylidenacetophenone, together with those observed for dibenzoylmethane and ethoxybenzylidenacetophenone, are as follows:

	$M_d$	$M_a$	$M_y$	$M_d$	$M_a$	$M_y$
Benzylidenacetophenone	79.4	75.3	79.4			
Replacement, H by OH (Benzyl alcohol—toluene)	1.4	1.4	1.4			
Estimated value for $\text{HO} \cdot \text{H} \cdot \text{O}$ $\text{Ph} \cdot \text{C}(\text{OH}) \cdot \text{C}(\text{OH}) \cdot \text{Ph}$				71.8	76.7	80.7
Observed value for dibenzoylmethane				74.6	81.5	88.0
Difference				2.8	4.8	7.3
Benzylidenacetophenone	79.4	75.3	79.4			
Replacement, H by OEt	19.6	19.7	19.8			
Estimated value for $\text{EtO} \cdot \text{H} \cdot \text{O}$ $\text{Ph} \cdot \text{C}(\text{OEt}) \cdot \text{C}(\text{OEt}) \cdot \text{Ph}$				81.0	86.0	90.1
Observed value for ethoxybenzylidenacetophenone				79.6	85.2	—
Difference				1.4	0.8	—

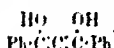
The differences between the observed and calculated values for ethoxybenzylidenacetophenone are within those allowed for the experimental error of the method used (2 per cent.), and there



is no marked increase in dispersion. The increase in dispersion and the magnitude of the difference in the case of dibenzoylmethane are, however, beyond those which can be regarded as due to experimental error. The estimated value for the diketone would be obviously much less than that for the hydroxy-ketone:

$$[2M.R., Ph.CO.Me - M.R., CH_3 = 72.0 - 6.6 = 65.4]$$

It was thought that a possible explanation might be found for the discrepancy by attributing a dienolic structure to dibenzoylmethane, which would then be represented as an allene derivative:



It was conceivable that if this represented the structure of dibenzoylmethane, its carboxyl derivative might show optical activity; the *para*-carboxyl derivative was prepared by condensing diethyl terephthalate with acetophenone in the presence of sodamide, and showed the red tinge characteristic of dibenzoylmethane; it melted at 95°. It was soluble in sodium hydroxide, and gave an intense red colour with ferric chloride. On hydrolysis, a pale yellow carboxyl compound, melting at 232°, was obtained. Its strychnine and cinchonine salts were prepared in a crystalline state from solution in methyl alcohol, but specimens of the acid prepared from successive fractions of the crystals obtained showed no trace of optical activity.

The refractive power of certain aliphatic allene derivatives was investigated by Brühl, who concluded that no exaltation of refractive power occurs such as accompanies the conjugation of two ethenoid linkings.

Tetraphenylallene was prepared by the distillation of barium diphenylacetate (Vorländer, *Ber.*, 1906, 39, 1024), and its refractive power examined. In preparing this substance, a mixture of two hydrocarbons at once crystallised from the oily distillate as Vorländer described; these were separated, and on leaving the remaining oil for some weeks, large, transparent plates, identified as tetraphenylacetone, were also obtained. These melted at 27-28°; no oxime could be obtained by prolonged boiling with hydroxylamine solution; this is probably an instance of the action of steric hindrances.

#### Molecular Refraction estimated for Tetraphenylallene.

	M <sub>a</sub>	
2M.R. as diphenylethylene, Ph <sub>2</sub> C=CH <sub>2</sub> . . . . . 2 ×		
69.1 . . . . .	120.2	
M.R., CH <sub>3</sub> . . . . .	6.6	
Observed value . . . . .		113.6
		117.7
Difference . . . . .		4.1

*Molecular Refraction estimated for Tetraphenylallene.*

The exaltation produced is therefore very much less than when double bonds enter into conjugation (compare Trans, 1908, 93, 373), and is insufficient to explain the high value found for the molecular refraction of dibenzoylmethane. From the data available the calculated values for the dienolic allene form and the hydroxy ketonic form of dibenzoylmethane do not greatly differ.

*Molecular Refraction estimated for Dihydroxydiphenylallene.*

	$M_d$	$M_R$
M. R. tetraphenylallene	111.7	124.5
$2 \text{ M. R. Ph}_2\text{C=CH}_2 - \text{M. R. Ph}_2\text{C=O}$	48.2	49.8
$2(\text{OH} - \text{H})$ .....	2.8	2.8
Observed value for dibenzoylmethane	72.5	77.5
Estimated value for hydroxy ketonic formula	74.6	81.5
	71.8	76.7

No evidence could therefore be obtained in favour of the existence of a dienolic form of dibenzoylmethane. It is probable that dibenzoylmethane does exist in the hydroxy ketonic form; a possible explanation of the abnormal refractive power may perhaps lie in the symmetry of the molecule and the consequent oscillation of a hydrogen between the two oxygen atoms. If this be so, the deviation should be less when substituents are introduced into one of the phenyl nuclei; but at present there is not sufficient evidence to show that the possibility of such an oscillation is attended with an exaltation of refractive power.

*Alkyl Derivatives of Dibenzoylmethane.*

The  $\alpha\alpha$ - and  $\beta\beta$ -dibenzoylpropanes were prepared, and their refractive powers examined. The molecular refractions of both are best in accordance with the diketonic structure.

*Molecular Refraction estimated for  $\beta\beta$ -Dibenzoylpropane.*

	$M_d$	$M_R$	$M_R^*$
M. R. $(2\text{Ph}\cdot\text{CO}\cdot\text{Me} + \text{C})$ .....	74.4		77.91
Observed: $\alpha\alpha$ -Dibenzoylpropane .....	74.98	78.40	79.37*
$\beta\beta$ -Dibenzoylpropane .....	75.99	78.25	—

*Action of Grignard's Reagent on the Aromatic  $\beta$ -Diketones.*

The application of Hibbert and Sudborough's method for the determination of the number of hydroxyl groups present in the aromatic  $\beta$ -diketones by observing the volume of gas liberated

when a known quantity of the substance is treated with a known amount of the Fehling reagent, gave results agreeing with the presence of an hydroxyl group in dibenzoylmethane and with a ketonic structure for dimethyldibenzoylmethane. In the case of benzoylacetone, the volume of gas evolved was about two-thirds of that required by theory for the hydroxy-ketonic structure.

A study of the products formed showed that  $\beta\beta$ -dibenzoylpropene reacts with magnesium methyl iodide, forming the tertiary alcohol  $C_6H_5CO\cdot CMe_2\cdot CMe(OH)\cdot C_6H_5$ . The chief product of the interaction of dibenzoylmethane and magnesium phenyl iodide was always the unchanged substance; a small amount of a pale yellow substance, melting at  $83^\circ$ , was obtained, analysis of which agreed with the formula  $C_6H_5CH_2CH\cdot CO\cdot C_6H_5$ .

#### EXPERIMENTAL.

*Benzoylacetone*.—This substance was obtained from Kahibaum and recrystallized from alcohol. Its refractive power was examined in chloroform solution.

Percentage strength of solution in $CHCl_3$	$M_D$	$M_D$	$M_D$
10.159	70.24	55.52	56.05

*Dibenzoylmethane*.—The dibenzoylmethane used was prepared by the condensation of ethyl benzoate and acetophenone in dry etheral solution under the influence of sodamide (Claisen, *Ber.*, 1905, 38, 693). The sodium compound was decomposed by gradually adding it to glacial acetic acid, precipitating by the addition of water, and recrystallizing from methyl alcohol and light petroleum. The crystals so obtained were always of a pink tinge, and melted at  $78^\circ$ .

Determination of refractive power in chloroform solution:

Percentage strength of solution.	$M_D$	$M_D$	$M_D$
3.2007	74.16	81.43	87.96
9.0734	74.56	81.45	—
3.0334	74.26	81.67	—
Mean . . . .	74.56	81.52	—

*Ethoxybenzylidenacetophenone*.—The starting point in preparing this substance was dibenzylidenacetophenone (Ruhemann and Watson, *Trans.*, 1904, 85, 456); in brominating this, the dibromide described by Wislicenus, melting at  $157$ – $158^\circ$ , was obtained, and in addition a stereoisomeric compound, melting at  $112$ – $113^\circ$  (*Proc.*, 1902, 25, 259).

The pale yellow crystals of ethoxybenzylidenacetophenone melted

at  $18^\circ$ ; their refractive power was determined in chloroform solution.

Percentage strength of solution.	$M_D$	$M_A$
1.5710	79.85	85.16
2.0607	79.25	—

*Preparation of p-Carboethoxydibenzoylmethane.*—Twenty-two grams of diethyl terephthalate and 11 grams of acetophenone were dissolved in dry ether, and 8 grams of sodamide gradually added. The mixture was surrounded by ice and kept overnight. The insoluble sodium compound which separated was collected, and decomposed with ice and glacial acetic acid; the product, when crystallised from methyl alcohol, melted at  $97-98^\circ$ . It was pink in colour, soluble in sodium hydroxide, and gave an intense red colour with ferric chloride.

0.973 gave 0.2600  $\text{CO}_2$  and 0.044  $\text{H}_2\text{O}$ .  $C = 72.88$ ;  $H = 5.03$ .

$\text{C}_{15}\text{H}_{12}\text{O}_4$  requires  $C = 72.97$ ;  $H = 5.40$  per cent.

*Hydrolysis.*—Twenty grams of the carboethoxy-compound were dissolved in boiling alcohol, a 10 per cent. solution of alcoholic potash added, and the mixture warmed on a water bath for from five to ten minutes. The yellow insoluble potassium salt which separated was dissolved in water, and the solution acidified with dilute hydrochloric acid. A pale yellow substance, melting at  $225^\circ$ , separated, which was very sparingly soluble in alcohol, but could be crystallised from ethyl acetate or from glacial acetic acid; it melted at  $232^\circ$  when recrystallised from ethyl acetate.

*Preparation of Tetraphenylacetone.*—From the oily distillate obtained by distilling barium diphenylacetate (Vorländer and Siebert, *Ber.*, 1906, **39**, 1024) under a pressure of 10 mm., there separated white crystals, which on recrystallisation from alcohol melted at  $166^\circ$ , and consisted of tetraphenylallene. The melting point of successive crops of crystals was lower, and consisted of a mixture of the two hydrocarbons described by Vorländer. The oily residue was kept for some weeks, and eventually crystallised, large, transparent, tabular plates being formed at the surface of the liquid. These melted at  $24-26^\circ$ , and on recrystallisation from dilute alcohol at  $27-28^\circ$ .

0.1104 gave 0.3634  $\text{CO}_2$  and 0.0585  $\text{H}_2\text{O}$ .  $C = 89.77$ ;  $H = 5.79$ .

$\text{C}_{27}\text{H}_{20}\text{O}$  requires  $C = 89.50$ ;  $H = 6.07$  per cent.

This substance is therefore the tetraphenylacetone which Vorländer and Siebert assumed to be first formed in the reaction, but which they did not then succeed in isolating.

A solution heated on a water-bath for twelve hours with a large

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excess of hydroxylamine appeared unchanged; the original substance was recovered, and no oxime could be detected.

## Refractive Power of Tetraphenylacetone.

Percentage of substance in chloroform solution	$M_D$	$M_A$
1.9417	115.5	119.3

## Refractive Power of Tetraphenylallene (m. p. 166°).

Percentage of substance in chloroform solution	$M_D$	$M_A$	$M_T$
1.7299	117.91	124.97	128.23
2.1545	117.55	124.9	125.9

## aa Dibenzoylpropane.

This substance cannot be directly prepared from dibenzoylmethane by ethylation; it was obtained (Auger, *Ann. Chim. Phys.*, 1891, [vi], 22, 351) by the action of aluminium chloride on a mixture of benzene and the dichloride of ethylmalonic acid, and the product purified by distillation under diminished pressure. The distillate remained for a long time as an oil which only gradually solidified after keeping for some days. It was purified by recrystallisation from alcohol and from petroleum, and eventually obtained in colourless needles, melting at 86–87°.

An attempt to prepare dibenzoylthane by condensing propiophenone and ethyl benzoate in dry ethereal solution in the presence of sodamide was not successful. An insoluble sodium compound is formed, which appears to be hydrolysed with extreme ease.

## Refractive Power of aa Dibenzoylpropane.

Percentage of substance in chloroform solution	$M_D$	$M_A$	$M_T$
3.5044	71.95	78.40	79.37

## BB Dibenzoylpropane.

This was prepared by condensing the dichloride of dimethylmalonic acid with benzene in the presence of aluminium chloride.

One hundred grams of dimethylmalonic acid and 170 grams of thionyl chloride were heated from three to four hours on a water-bath, and the product then distilled under diminished pressure. Forty grams of the dichloride thus obtained were dissolved in 400 c.c. of benzene, and 60 grams of aluminium chloride gradually added. The mixture was kept overnight, and then heated for two hours on a water-bath. After distilling off the excess of benzene,

the warm product was poured into water and extracted with ether. The excess of ether was evaporated and light petroleum added to the concentrated ethereal solution, when colourless needles separated. These, when recrystallised from light petroleum, melted at  $99^\circ$ , and gave no red coloration with ferric chloride:

0.1238 gave 0.3640  $\text{CO}_2$  and 0.0730  $\text{H}_2\text{O}$ .  $\text{C} = 80.19$ ;  $\text{H} = 6.55$ .

$\text{C}_{17}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 80.95$ ;  $\text{H} = 6.35$  per cent.

*Refractive Power of  $\beta\beta$ -Dibenzoylpropane.*

Percentage of substance in  
chloroform solution.

5.1545

$M_D$

75.99

$M_A$

78.25

*Action of Grignard Reagent on  $\beta\beta$ -Dibenzoylpropane.*

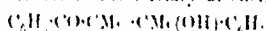
To an ethereal solution of 1 gram of magnesium and 6 grams of methyl iodide, an ethereal solution of 5 grams of  $\beta\beta$ -dibenzoylpropane was added. After keeping overnight, the product was decomposed, first with ice-water, and then with 30 per cent. sulphuric acid. The solution was extracted with ether, and the product distilled under diminished pressure.

A fraction boiling between  $120^\circ$  and  $125^\circ$  5 mm. was obtained, which gave a red colour with ferric chloride:

0.0867 gave 0.2555  $\text{CO}_2$  and 0.0593  $\text{H}_2\text{O}$ .  $\text{C} = 80.3$ ;  $\text{H} = 7.6$ .

$\text{C}_{17}\text{H}_{18}\text{O}_3$  requires  $\text{C} = 80.60$ ,  $\text{H} = 7.44$  per cent.

The product is therefore the tertiary alcohol,



*Estimation of Hydroxyl Groups Present in the Aromatic  $\beta$ -Diketones.*

A solution of magnesium methyl iodide in amyl ether was used as described by Hibbert and Sudborough (Trans., 1904, 85, 933). This reagent, together with a weighed quantity of the substance, was introduced into a flask, and the volume of gas evolved measured in a nitrometer:

Substance.	Weight, gram.	Volume of gas evolved (N.T.P.) c.c.	Volume corresponding with presence of one hydroxyl- group in the molecule.
			c.c.
$\beta\beta$ -Dibenzoylpropane	0.144	0.0	—
	0.130	0.0	—
Dibenzoylmethane	0.2168	19.32	21.5
	0.256	25.4	25.4
Benzoylacetone	0.4224	36.2	38.0
	0.183	17.6	23.1

*Action of Magnesium Phenyl Bromide on Dibenzoylmethane.*

2.4 Grams of magnesium were treated with 21 grams of bromobenzene in dry ethereal solution, and the product was added to an ethereal solution containing 10 grams of dibenzoylmethane. After keeping overnight, the product was heated for six hours on a steam-bath. After decomposing with ice and with 30 per cent sulphuric acid, the product, after extracting with ether, was distilled under a pressure of 20 mm. The fraction boiling between  $200^{\circ}$  and  $230^{\circ}$  was dissolved in alcohol, and deposited pink crystals of dibenzoylmethane and pale yellow crystals; the latter were separated mechanically and recrystallized from alcohol. They melted at  $89^{\circ}$ , and gave the following result on analysis:

0.1151 gave 0.3732 (CO), and 0.0637  $H_2O$ . C: 88.44; H: 6.17

$C_{12}H_{10}O$  requires C: 88.74; H: 5.63 per cent

The substance gave no red coloration with ferric chloride, and was insoluble in alkali. It was therefore probably  $\beta$ -benzoyl- $\alpha$ -diphenylethylene. The yield was exceedingly poor, most of the dibenzoylmethane being recovered unchanged.

In a subsequent experiment, in which an excess of magnesium phenyl bromide (2.4 grams of magnesium and 30 grams of bromobenzene) was added to an ethereal solution of 5 grams of dibenzoylmethane, a very small quantity of yellow crystals, melting at  $188^{\circ}$ , was obtained, the amount was not sufficient for investigation.

Much of the expense of this investigation has been met by a grant from the Research Fund Committee of the Chemical Society.

THE UNIVERSITY,  
MANCHESTER.

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# ERRATA.

## VOL. XCVII (TRANS., 1910).

Page	Line	
55	19	for " $C_{24}H_{24}O_4N_2S_2$ " read " $C_{24}H_{24}O_6N_2S_2$ ."
56	10	" " $C_{24}H_{24}O_6N_2S_2$ " " " $C_{24}H_{24}O_6N_2S_2$ ."
60	13*	" " $C_{12}H_8O_4N_2S_2$ " " " $C_{22}H_{12}O_6N_2S_2$ ."
82	1	" "3:6-Dibenzoyl-9-phenylzanthen." read "3:6-Dibenzoyloxy-9-phenylzanthen."
464	2*	" " $C_{22}H_{17}O_2NS$ " read " $C_{22}H_{17}O_2NS$ ."
690	12	" " $C_{15}H_4O_3Cl_2$ " " " $C_{15}H_4O_3Cl_2$ ."

## VOL. XCVIII (ABSTR., 1910).

311	1*	for "Abstr., 1909, i, 4" read "this vol., i, 4."
i, 330	2	" "HENRICHSEN" read "HINRICHSEN."
i, 351	8	" "932" read "934."
i, 357	6	" "ethyl anilino." read "ethyl anilino."
i, 371	14*	" "2:4-Dinitrophenyl-dl-leucine" read "Chloro-2:4-dinitro-dl-leucine."
i, 376	11*	" " $C_6H_4 \begin{array}{c} \text{CH} \\   \\ \text{C(OH)} \end{array} \text{C}_6H_4(OH)_2 \cdot SO_3Na$ " read " $C_6H_4 \begin{array}{c} \text{CH} \\   \\ \text{C(OH)} \end{array} \text{C}_6H_4(OH)_2 \cdot SO_3Na$ ."
i, 433	17	" "u-Bromo." read "u-Chloro."
ii, 250	20	" "23-32" read "23-37."
ii, 381	11	" "BAUER" read "BAUR."
ii, 410	3	" "1910" read "1909."
ii, 572	25	" "in water vapour" read "as water vapour."
ii, 578	25	" "effect" read "affect."
ii, 581	9	" " $\beta\gamma$ " read " $\beta\gamma$ ."
ii, 581	18	" " $A = -T \sqrt{Q/T_d T}$ " read " $A = -T \int Q T_d T$ ."

\* From bottom.

the warm product was poured into water and extracted with ether. The excess of ether was evaporated and light petroleum added to the concentrated ethereal solution, when colourless needles separated. These, when recrystallised from light petroleum, melted at  $99^{\circ}$ , and gave no red coloration with ferric chloride:

0.1238 gave 0.3640  $\text{CO}_2$  and 0.0730  $\text{H}_2\text{O}$ .  $\text{C}=80.19$ ;  $\text{H}=6.55$ .

$\text{C}_{17}\text{H}_{16}\text{O}_2$  requires  $\text{C}=80.95$ ;  $\text{H}=6.35$  per cent.

#### *Refractive Power of $\beta\beta$ -Dibenzoylpropane.*

Percentage of substance in  
chloroform solution.

5.1545

$M_a$ .

75.99

$M_g$ .

78.25

#### *Action of Grignard Reagent on $\beta\beta$ -Dibenzoylpropane.*

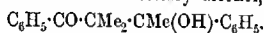
To an ethereal solution of 1 gram of magnesium and 6 grams of methyl iodide, an ethereal solution of 5 grams of  $\beta\beta$ -dibenzoylpropane was added. After keeping overnight, the product was decomposed, first with ice-water, and then with 30 per cent. sulphuric acid. The solution was extracted with ether, and the product distilled under diminished pressure.

A fraction boiling between  $120^{\circ}/55$  mm. was obtained, which gave a red colour with ferric chloride:

0.0867 gave 0.2555  $\text{CO}_2$  and 0.0593  $\text{H}_2\text{O}$ .  $\text{C}=80.3$ ;  $\text{H}=7.6$ .

$\text{C}_{16}\text{H}_{20}\text{O}_2$  requires  $\text{C}=80.60$ ;  $\text{H}=7.44$  per cent.

The product is therefore the tertiary alcohol,



#### *Estimation of Hydroxyl Groups Present in the Aromatic $\beta$ -Diketones.*

A solution of magnesium methyl iodide in amyl ether was used as described by Hibbert and Sudborough (Trans., 1904, **85**, 933). This reagent, together with a weighed quantity of the substance, was introduced into a flask, and the volume of gas evolved measured in a nitrometer:

Substance.	Weight, gram.	Volume of gas evolved (N.T.P.) c.c.	Volume corresponding with presence of one hydroxyl group in the molecule.
			c.c.
$\beta\beta$ Dibenzoylpropane .....	0.144	0.0	—
	0.130	0.0	—
Dibenzoylmethane .....	0.2163	19.32	21.5
	0.256	25.4	25.4
Benzoylacetone .....	0.4224	30.2	58.0
	0.183	17.6	26.1



*Action of Magnesium Phenyl Bromide on Dibenzoylmethane.*

2.4 Grams of magnesium were treated with 21 grams of bromobenzene in dry ethereal solution, and the product was added to an ethereal solution containing 10 grams of dibenzoylmethane. After keeping overnight, the product was heated for six hours on a steam-bath. After decomposing with ice and with 30 per cent. sulphuric acid, the product, after extracting with ether, was distilled under a pressure of 20 mm. The fraction boiling between 200° and 230° was dissolved in alcohol, and deposited pink crystals of dibenzoylmethane and pale yellow crystals; the latter were separated mechanically and recrystallised from alcohol. They melted at 89°, and gave the following result on analysis:

0.1151 gave 0.3732 CO<sub>2</sub> and 0.0637 H<sub>2</sub>O. C=88.44; H=6.17.

C<sub>21</sub>H<sub>10</sub>O requires C=88.74; H=5.63 per cent.

The substance gave no red coloration with ferric chloride, and was insoluble in alkali. It was therefore probably  $\beta$ -benzoyl- $\alpha\alpha$ -diphenylethylene. The yield was exceedingly poor, most of the dibenzoylmethane being recovered unchanged.

In a subsequent experiment, in which an excess of magnesium phenyl bromide (2.4 grams of magnesium and 30 grams of bromobenzene) was added to an ethereal solution of 5 grams of dibenzoylmethane, a very small quantity of yellow crystals, melting at 188°, was obtained; the amount was not sufficient for investigation.

Much of the expense of this investigation has been met by a grant from the Research Fund Committee of the Chemical Society.

THE UNIVERSITY,  
MANCHESTER.

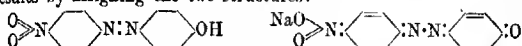
### CCXXXVIII.—*The Relation between Absorption Spectra and Chemical Constitution. Part XV. The Nitro- and Azo-compounds.*

By EDWARD CHARLES CYRIL BALY, WILLIAM BRANSHAW TUCK, and  
EFFIE GWENDOLINE MARSDEN.

In a recent paper (this vol., p. 571), we described the results of an investigation of the absorption spectra of a number of aromatic nitro-compounds, and showed that the absorption and colour of these substances is to be explained by the isorropesis between the residual affinity of the nitro-group and that of the phenyl or substituted phenyl residue. We pointed out that the quinonoid theory is entirely unnecessary, and in some cases impossible of

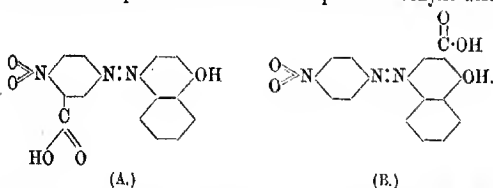
acceptance, since it fails in the case of the meta-nitro-derivatives. The quinonoid explanation has received considerable support from a series of investigations by Hewitt and his co-workers on certain nitroazo-compounds. We have examined the same compounds as described by Hewitt, and we find that our results do not support the quinonoid hypothesis, but are very strongly in favour of the explanation put forward in our previous paper.

In the first place Hewitt and Mitchell (Trans., 1907, 91, 1251) deal with the *p*-nitroazophenols, and show that the colour of these compounds changes from yellow to red when they are converted into their alkali metal salts, whilst *p*-nitrobenzene-4-azo- $\alpha$ -naphthol, itself a red substance, gives blue alkali salts. The neutral and alkaline solutions, they say (p. 1255), exhibit absorption of radically different type, except where the presence of inhibiting groups prevents the formation of the diquinonoid structure. They interpret their results by assigning the two structures:

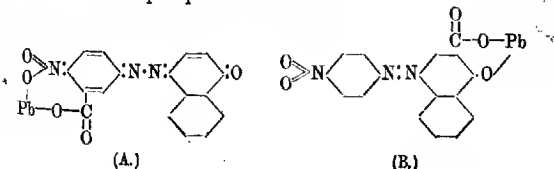


respectively to the parent substance and the sodium salt. Moreover, they say that the parent compound in *N*/500-solution exhibits only general absorption from  $\lambda=500\mu$ , whilst the potassium salt in *N*/20,000-solution exhibits an absorption band between  $\lambda=532\mu$  and  $\lambda=485\mu$ .

A further argument which they bring forward in support of their view that the alkali salts are quinonoid is the relative behaviour of the two isomeric *p*-nitrobenzene-4-azo- $\alpha$ -naphtholcarboxylic acids:



Both these compounds give blue solutions in the presence of sodium hydroxide, but compound A gives a blue precipitate with lead acetate, whilst B gives a red precipitate. Hewitt and Mitchell attribute to these precipitates the formulae:



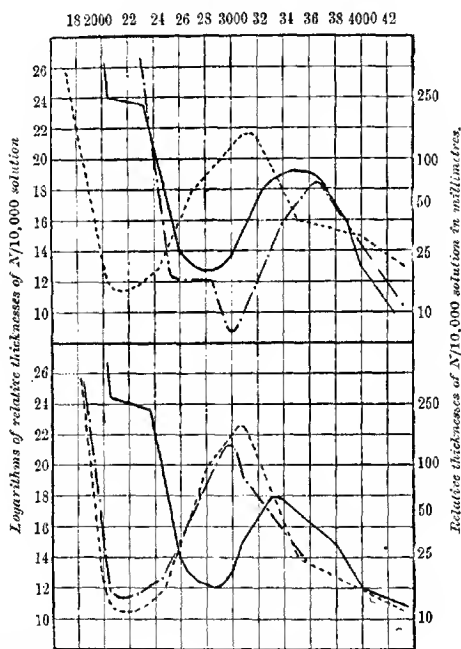
As the result of our investigations, we do not agree with Hewitt and Mitchell that there is a radical difference between the absorption of the nitroazophenols and their sodium salts, or between the

FIG. 1.

Upper curves :

Full curve : *o*-Nitrobenzenazophenol in alcohol.  
Dotted curve : *o*-Nitrobenzenazophenol in alcoholic NaOEt.  
Dot and dash curve : *p*-Benzquinoneazaline.

Oscillation frequencies.



Lower curves :

Full curve : *m*-Nitrobenzenazophenol in alcohol.  
Dotted curve : *m*-Nitrobenzenazophenol in alcoholic NaOEt.  
Dot and dash curve : *m*-Nitrobenzenazodimethylaniline in alcohol.

nitroazonaphthols and their sodium salts. The absorption curves of the two classes of compounds are shown in Figs. 1, 2, and 3, and it may be seen that the absorption with and without alkali is of

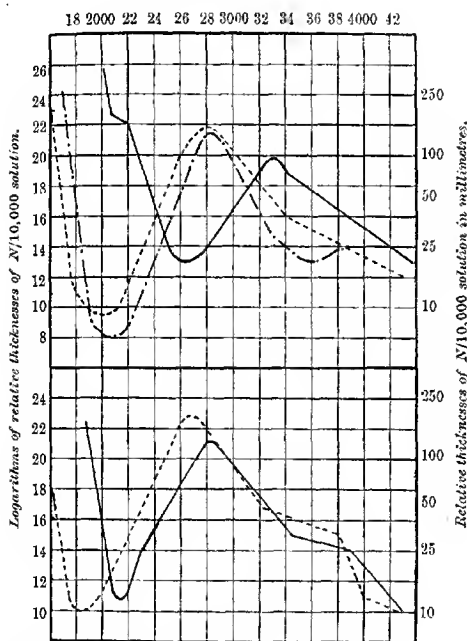
exactly the same type, the only difference being that there is a shift towards the red on the addition of the alkali. This is exactly similar to the shift observed with the nitrophenols, and is capable

FIG. 2.

Upper curves:

- Full curve: *p*-Nitrobenzenesazophenol in alcohol.  
Dotted curve: *p*-Nitrobenzenesazophenol in alcoholic NaOEt.  
Dot and dash curve: *p*-Nitrobenzenesazodimethylaniline in alcohol.

Oscillation frequencies.



Lower curves:

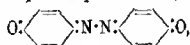
- Full curve: *o*-Nitrobenzenesazo-*a*-naphthol in alcohol.  
Dotted curve: *o*-Nitrobenzenesazo-*a*-naphthol in alcoholic NaOEt.

of the same explanation, namely, that it is due to the shift which occurs when alkali is added to a solution of phenol itself. If Hewitt and Mitchell had examined *p*-nitrobenzenesazophenol at the same strength as its potassium salt, they would also have found an

absorption band. Exactly the same shift is to be observed with benzeneazophenol as has been previously shown by one of us (Tuck, Trans., 1907, 91, 450).

We have examined the absorption spectra of the three isomeric nitrobenzeneazophenetoles, and find them identical with those of the corresponding nitrobenzeneazophenols. The absorption spectra of the nitrobenzeneazodimethylanilines were also investigated; only the *m*- and *p*-isomerides were prepared, and it was found that their absorption is very similar to that of the corresponding sodium nitrobenzeneazophenoxides (see Figs. 1 and 2). Since it is, of course, impossible for the former compounds to be quinonoid, this similarity argues strongly against the quinonoid structure of the sodium salts of the nitroazophenols.

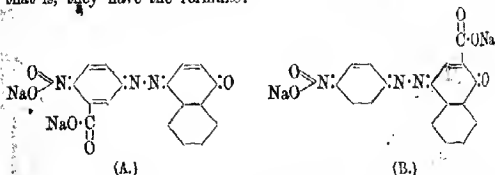
In order to obtain conclusive evidence, we have examined the absorption spectrum of *p*-benzoquinoneazine,



which contains the diquinonoid linking exactly as is claimed by Hewitt and Mitchell for the sodium salt of *p*-nitrobenzeneazophenol. The curve is shown in Fig. 1, and, as can be seen, bears no resemblance to any of the nitroazophenol curves. It is evident therefore that the latter compounds cannot be quinonoid.

In reference to *p*-benzoquinoneazine, a very striking resemblance exists between its absorption and those of the *o*-hydroxyazo-compounds which one of us, from observations of their absorption spectra, concluded were quinonehydrazones (Tuck, *loc. cit.*). The result given by benzoquinoneazine is additional evidence in favour of this conclusion.

Turning to the two isomeric *p*-nitrobenzeneazo- $\alpha$ -naphthol-carboxylic acids mentioned above, it appears to us that the argument of Hewitt and Mitchell is fallacious. Both acids are blue in alkaline solution, and therefore, according to their view, both are quinonoid, that is, they have the formulæ:



Now, in A it is true that there are two neighbouring ONa groups which may give a lake, but this is not the case in B, for the two ONa groups are at opposite ends of the molecule. It is therefore impossible for Hewitt and Mitchell's lake formation to take place

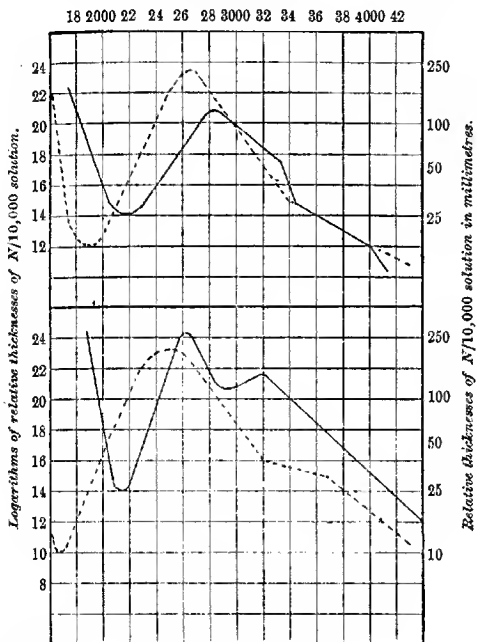
Fig. 3.

Upper curves :

 Full curve : *m*-Nitrobenzenazo- $\alpha$ -naphthol in alcohol.

 Dotted curve : *m*-Nitrobenzenazo- $\alpha$ -naphthol in alcoholic NaOEt.

Oscillation frequencies.

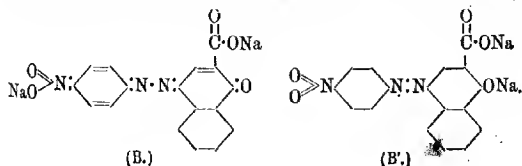


Lower curves :

 Full curve : *p*-Nitrobenzenazo- $\alpha$ -naphthol in alcohol.

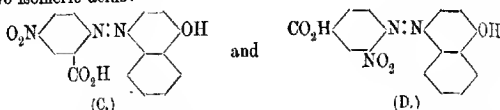
 Dotted curve : *p*-Nitrobenzenazo- $\alpha$ -naphthol in alcoholic NaOEt.

in B unless the Na attached to the  $\text{NO}_2$  group were tautomeric. If it were labile, then the two forms B and B' would be in equilibrium :



But the whole essence of the argument depends on there not being any such equilibrium in existence, for if an equilibrium did exist it would be impossible to attribute a definite reaction, such as lake formation, to one phase and one phase only. It appears therefore to us that Hewitt and Mitchell's deduction of the quinonoid structure from the lake formation is unsound.

Now, we have prepared and investigated the properties of the two isomeric acids:



and we find that C, which is blue in alkaline solution, also gives a blue precipitate with lead acetate, whilst D, which is purple in alkaline solution, gives a purple precipitate with barium chloride. As in neither case are there two adjacent hydroxyl groups, it follows that the formation of insoluble "lakes" cannot in any way be taken as evidence of there being two such adjacent groups.

We have further investigated the reactions of the above two acids (C and D) and also of Hewitt and Mitchell's acid (B), and we find that various coloured precipitates can be obtained with the greatest ease according to the strength of the solution. The explanation lies in the fact that the sodium salts of the three acids form colloidal solutions and may be precipitated at once by the addition of *any metallic salt*. For example, if to a strong aqueous solution of the sodium salt of Hewitt and Mitchell's acid (B) a few drops of an aqueous solution of sodium chloride be added, the sodium salt is thrown down as an insoluble *blue* precipitate. If, on the other hand, a dilute solution of the sodium salt be used, the addition of the sodium chloride solution turns it red, and in a few moments the acid itself is thrown down as a *red* precipitate. Exactly the same is true in the case of the two isomeric acids A and B above. It appears therefore that no evidence whatever as regards structure can be obtained from the behaviour of these acids with lead acetate. The evidence obtained from the absorption spectra is overwhelmingly against the quinonoid configuration of the nitrobenzenediazophenols and  $\alpha$ -naphthols, and we therefore attribute the same explanation as was put forward in our previous paper, namely, that the absorption is due to the association of the residual affinities of the nitrophenyl, azo, and phenol or naphthol groupings, and that the shift of the absorption band on the addition of alkali is due to the same cause as the shift in the absorption of phenol itself when alkali is added. It may be seen from the figures that in the case of the nitrobenzenediazophenols the shifts produced by

the addition of alkali to the ortho-, meta-, and para-isomerides are 670, 700, and 600 units respectively. In the case of the corresponding naphthols, the shifts are 280, 300, and 470 units respectively. The shift therefore given by the meta-isomeride is of the same order as those given by the ortho- and para-isomerides.

# EXPERIMENTAL.

*o*-Nitrobenzeneazophenetole.—This was prepared by boiling *o*-nitrobenzeneazophenol in alcoholic solution with ethyl bromide and sodium ethoxide for about one hour. The ether crystallises from dilute alcohol in small, flat, bronze needles, melting at 88°:

0.1195 gave 16.0 c.c.  $N_2$  (moist) at 19° and 764.2 mm.  $N=15.52$ .

$C_{14}H_{13}O_3N_3$  requires  $N=15.5$  per cent.

*m*-Nitrobenzeneazophenetole.—Prepared in the same way as the ortho-isomeride. Crystallises from alcohol in flat, yellow needles, melting at 96°:

0.1194 gave 16.1 c.c.  $N_2$  (moist) at 18° and 761.2 mm.  $N=15.64$ .

$C_{14}H_{13}O_3N_3$  requires  $N=15.5$  per cent.

*p*-Nitrobenzeneazophenetole.—Prepared in the same way as the two preceding compounds. Crystallises from alcohol in very small, dark yellow needles, melting at 155°:

0.1153 gave 15.4 c.c.  $N_2$  (moist) at 16° and 747.2 mm.  $N=15.63$ .

$C_{14}H_{13}O_3N_3$  requires  $N=15.5$  per cent.

*o*-Nitro-*o*-carboxybenzene-4-azo- $\alpha$ -naphthol.—This was prepared by diazotising 3-nitro-4-aminobenzoic acid with amyl nitrite, and pouring the resulting solution into the  $\alpha$ -naphthol dissolved in sodium hydroxide. The sodium salt was decomposed by dilute sulphuric acid, and steam was passed through the mixture for half an hour. The azo-compound was recrystallised from nitrobenzene. It forms red, microscopic needles, which melt and decompose at 313°:

0.1209 gave 13.2 c.c.  $N_2$  (moist) at 24° and 758 mm.  $N=12.25$ .

$C_{17}H_{11}O_5N_3$  requires  $N=12.46$  per cent.

The 3-nitro-4-aminobenzoic acid was prepared from aceto-*p*-toluidide. This was nitrated by slowly adding it to nitric acid (D 1.45). The nitro-compound was then oxidised by suspension in water through which a current of steam was led, while finely powdered potassium permanganate (2 mols.) was added in small quantities exactly as described by Hewitt and Mitchell. The resulting nitro-acetylaminobenzoic acid was hydrolysed in the following way. To a boiling concentrated solution of the acid in alcohol, an equal volume of concentrated aqueous hydrochloric acid was added, and the mixture boiled for about one minute. The



nitroaminobenzoic acid then began to crystallise in well-formed needles, and, on cooling and adding water, the acid was obtained in a very pure state. The yield is almost quantitative.

*p*-Nitro-*o*-carboxybenzene-4-azo- $\alpha$ -naphthol.—This was prepared by diazotising 5-nitro-2-aminobenzoic acid, and pouring into a solution of  $\alpha$ -naphthol. The compound was recrystallised from nitrobenzene. It forms chocolate, microscopic needles, which melt and decompose at 303°:

0.1350 gave 14.4 c.c.  $N_2$  (moist) at 22° and 766.2 mm.  $N = 12.23$ .

$C_{17}H_{11}O_3N_3$  requires  $N = 12.46$  per cent.

The 5-nitro-2-aminobenzoic acid was prepared in two ways. The first quantity was obtained from aceto-*o*-toluidide by nitration and subsequent oxidation by potassium permanganate to 5-nitro-2-acetylaminobenzoic acid. The acetyl-amino-compound was hydrolysed in the same way as described above. The yield of the acetylaminocompound was, however, very poor, and a second quantity was prepared by direct nitration of acetylanthranilic acid; 75 grams were slowly added to 150 grams of nitric acid ( $D = 1.49$ ), and then kept for two hours. This period was found to be absolutely necessary. The mixture was then poured on ice; the yield of the nitro-compound is about 85 per cent.

We wish, in conclusion, to express our thanks to the Chemical Society for a grant in aid of this work.

SPECTROSCOPIC LABORATORY,  
UNIVERSITY OF LONDON,  
UNIVERSITY COLLEGE.

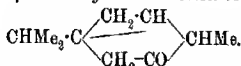
#### CXXXIX.—*A Contribution to the Study of Tanacetone ( $\beta$ -Thujone) and some of its Derivatives.*

By DAVID THOMSON (late 1851 Exhibition Research Scholar).

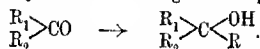
THE present paper contains a brief summary of the experimental work described in the author's dissertation (Göttingen, 1909). The work was carried out between October, 1907, and March, 1909, in Göttingen, under the supervision of Geh. Reg. Rat. Prof. Dr. O. Wallach, to whom the author desires to express his grateful thanks. The experiments had a twofold object in view: first, the chemical and optical study of tanacetone ( $\beta$ -thujone) and some of its derivatives; secondly, the preparation of a series of active compounds, the study of which seemed likely to throw some light on

the problem of the relationship between optical activity and chemical constitution. In this paper only the experimental data are given. A discussion of the optical data bearing on the question of optical activity and chemical constitution is reserved for a subsequent paper, when some experiments, at present in progress, on the condensation products of active 1-methylcyclohexan-3-one have been completed.

*Application of the Grignard Reaction to Tanacetone,*

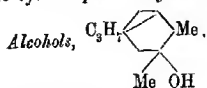


The application of the Grignard reagent to a ketone yields, as is well known, a tertiary alcohol according to the equation:

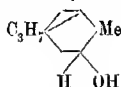


When R, R<sub>1</sub>, R<sub>2</sub> are all different, as with tanacetone, the carbon atom to which these groups are attached becomes asymmetric in the process. Since tanacetone is optically active, two tertiary alcohols must be expected with the rotations +A+B and +A-B respectively, where A denotes the rotation of tanacetone and  $\pm B$  that of the new asymmetric carbon atom. These two alcohols will not, however, be optical antipodes, and hence may be capable of mechanical separation. This proved to be the case. Tanacetone treated with magnesium methyl iodide yielded two tertiary alcohols, one liquid and one solid, which could be easily separated by cooling in a freezing mixture. The liquid alcohol boils at 202–205°, and has the specific rotation +35.8° ( $p=5.226$  in ether); the solid alcohol melts at 84°,  $[\alpha]_D -30.5^\circ$  ( $p=4.058$  in ether). The observation of rotatory power for the liquid alcohol is probably low, as it is unlikely that a complete separation of the solid alcohol was effected by the freezing-out process.

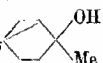
As the separation of the two isomeric homothujyl alcohols had proved so easy, the method was tried with the higher homologues, namely, the ethyl-, propyl-, and isopropyl-thujyl alcohols, but without success. The product of the Grignard reaction was in each case an oil which could not be separated into its isomeric constituents. Some isothujone, with which Prof. Wallach kindly furnished the author, on treatment with magnesium methyl iodide, gave a similar result. Separation of the oily reaction product into its two isomeric constituents proved an insuperable difficulty. In all these cases the absence of unattacked tanacetone was proved by treatment with semicarbazide solution.

*Stability of the cycloPropane Ring in the two Homothujyl*

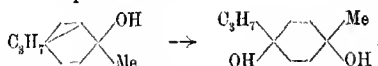
As this question has already been discussed by Wallach (*Annalen*, 1908, 360, 86), the results of the experiments need only be mentioned here. Both alcohols, like thujyl alcohol,



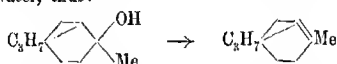
are not affected by long shaking with 5 per cent. sulphuric acid. Very different is the behaviour of the similarly constituted

sabinene hydrate, . By the same treatment it

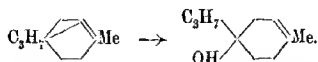
is converted into *p*-menthan-1:4-diol:



Wallach (*loc. cit.*) shows that the formation of this dihydric menthane does not take place directly, but indirectly, from  $\Delta^2$ -*p*-menthen-4-ol; and he finds in this intermediate product the clue to the difference in stability of the cyclopropane ring in sabinene hydrate and in thujyl and homothujyl alcohol. He assumes that the first action of the dilute sulphuric acid is to eliminate water, thus:



a reaction rendered all the easier by the mobility of the hydrogen atom attached to the tertiary carbon atom. The formation of the quaternary carbon atom, however, so weakens the stability of the cyclopropane ring that combination with water takes place at once, thus:

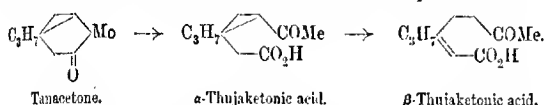


In the case of thujyl and the homothujyl alcohols, the formation of a double bond in immediate juxtaposition to the cyclopropane ring is hindered by the position of the hydroxyl group; hence the greater stability of these compounds. This explanation suffices to

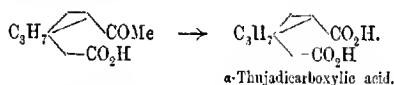
explain the behaviour of a great many terpenes towards dilute sulphuric acid, and we shall see presently that it is capable of application to the acids derived from tanacetone by oxidation.

*Oxidation Products of Tanacetone (β-Thujaone).*

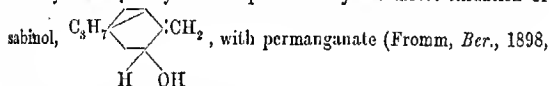
Wallach (*Annalen*, 1893, 272, 113; 1904, 336, 266) has shown that when tanacetone is oxidised with a neutral solution of 5 per cent. permanganate, a mixture of two ketonic acids, distinguished as α- and β-thujaketonic acid, is produced. The α-acid is saturated and optically active; the β-acid is unsaturated and optically inactive. The formation of these acids from tanacetone is explained thus:



The α-acid may be readily converted into the β-acid by distillation (Wallach, *Annalen*, 1893, 275, 166). Both the α- and the β-acids, when further oxidised with sodium hypobromite, yield the corresponding dicarboxylic acids (Semmler, *Ber.*, 1892, 25, 3348), for example:



α-Thujadicarboxylic acid—called by Semmler α-tanacetonedicarboxylic acid—may also be produced by the direct oxidation of



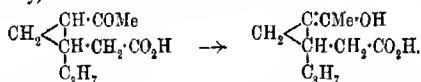
Several hundred grams of both α-thujaketonic and α-thujadicarboxylic acid were prepared.

The method adopted in the preparation of α-thujaketonic acid was, with but slight modification, that of Wallach (*loc. cit.*). Curiously enough, and in apparent contradiction to the result cited, it was found that whether the oxidation was carried out with warm or cold permanganate solution only one acid, namely, the α-acid, was produced. As the two ketonic acids are sharply distinguished in crystalline form—the α-acid crystallising in plates, the β-acid in needles—and in solubility, and as a careful watch was kept for any appearance of β-acid, its presence could scarcely have escaped detection. Whether this result is to be ascribed to some difference

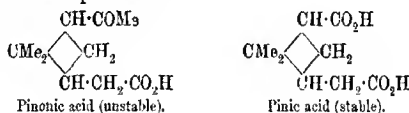
in the tanacetone, used or to the omission of the distillation in steam of the product of oxidation—which was the essential variation of Wallach's method adopted—is not yet quite clear.

*Stability of the cycloPropane Ring in  $\alpha$ -Thujaketonic and  $\alpha$ -Thujadicarboxylic Acids.*

Very remarkable is the difference in stability of the cyclopropane ring in  $\alpha$ -thujaketonic and  $\alpha$ -thujadicarboxylic acid. The ketonic acid is rapidly decomposed by boiling 20 per cent. hydrochloric acid, with formation of an inactive unsaturated hydrocarbon, which has the characteristic odour of dihydro- $\psi$ -cumene, and boils at  $160$ – $165^\circ$  (dihydro- $\psi$ -cumene boils at  $160^\circ$ ). The dicarboxylic acid is not affected in rotation and melting point by two hours' vigorous boiling with 20 per cent. hydrochloric acid, and shows a like stability towards boiling 10 per cent. sodium hydroxide. If one accepts the above explanation given by Wallach for the difference in stability of sabinene hydrate and homothujyl alcohol, the difference in stability of these two acids presents no difficulty. The first effect of the boiling hydrochloric on the ketonic acid is, presumably, to convert it into its enolic form:



The formation of the quaternary carbon atom, however, so diminishes the stability of the cyclopropane ring that decomposition at once takes place. With the dicarboxylic acid, on the other hand, such enolisation is impossible; hence its greater stability. Similar results were obtained by von Baeyer (*Ber.*, 1896, 29, 326) with pinonic and pinic acids:



*Esterification of  $\alpha$ -Thujadicarboxylic Acid.*

The great stability of  $\alpha$ -thujadicarboxylic acid towards hydrochloric acid having been proved, the esterification of this acid in the ordinary way by passing hydrogen chloride into the alcoholic solution of the acid was successfully attempted. Dimethyl, diethyl, di-*n*-propyl, diisobutyl, and diisooamyl esters were so prepared. The dimethyl and diethyl esters were easily obtained in a pure state; the esters of the other three alcohols were, as the boiling

points and the results of analysis indicate, never quite free from traces of impurity, most likely acid esters. An attempt to prepare a dibenzyl ester gave a compound which the results of analysis indicate to be a monobenzyl ester.

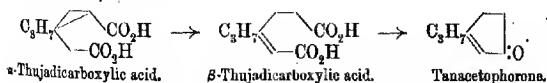
All these esters are clear, odourless, more or less viscous liquids. The absence of odour is rather remarkable. With the exception of the monobenzyl ester, which is pale yellow, they are quite colourless. They are very stable compounds, and do not give acid amides when shaken with a strong solution of ammonia. The methyl and ethyl esters were saponified, and the acid recovered. Melting point and rotatory power were unchanged. Hence there was no racemisation during the process of esterification.

The constants for these esters are given in the subjoined table. Details will be found in the experimental part. The boiling points were taken under a pressure of 10–14 mm.; the temperature at which the densities were taken also varied from 15° to 20°; hence the figures are not exactly comparable:

	B. p. (10–14 mm.)	$d_{15-20}^{20}$	$[\alpha]_D^{20}$
Dimethyl ester .....	126–127°	1.0535	+142.5°
Diethyl ester .....	138–140	1.019	114.1
Di-n-propyl ester .....	157–160	0.9969	84.7
Diisobutyl ester .....	174–177	0.9908	77.6
Dibenzamyl ester .....	187–190	0.9924	73.5
Monobenzyl ester (?) .....	215–220	—	34.7

*Decomposition Products of the Sodio-derivatives of the Dimethyl (and Diethyl) Esters of  $\alpha$ -Thujadicarboxylic Acid.*

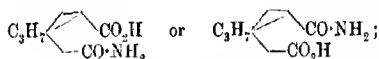
The dimethyl and diethyl esters of  $\alpha$ -thujadicarboxylic acid in solution in dry ether react slowly with metallic sodium, giving a sodio-derivative. An attempt to replace the sodium atom by an ethyl group failed, owing to the instability of the compound formed. On warming the sodio-derivative of the dimethyl (or diethyl) ester with water, and distilling the reaction mixture in a current of steam, an excellent yield of tanacetophorone was obtained. The tanacetophorone prepared in this way is much purer than that obtained by the distillation of thujadicarboxylic acid over soda-lime. The formation of tanacetophorone by the latter process depends, according to Semmler (*Ber.*, 1893, 25, 3350), on the conversion of  $\alpha$ -thujadicarboxylic acid into  $\beta$ -thujadicarboxylic acid, which then loses carbon dioxide and undergoes intramolecular condensation, thus:



If this explanation held in the present instance, then  $\beta$ -thuja-

dicarboxylic acid was to be expected among the residues in the distilling flask. Careful examination did reveal an inactive acid, the melting point of which was identical with that of  $\beta$ -thujadicarboxylic acid, namely, 116–117°. Along with it, and in slightly greater quantity, was another inactive acid, which melted at 150–151°, or nine degrees higher than  $\alpha$ -thujadicarboxylic acid. The nature of this acid has not yet been determined with certainty. Analysis proves it to be isomeric with the  $\alpha$ - and  $\beta$ -dicarboxylic acids. It is probably racemic  $\alpha$ -thujadicarboxylic acid.

*Monoamide of  $\alpha$ -Thujadicarboxylic Acid.*—The anhydride of  $\alpha$ -thujadicarboxylic acid reacts readily with ammonia, aniline, or piperidine. The additive product with piperidine is a liquid, with aniline, a glass. With ammonia, after some difficulty, a well-defined crystalline *monoamide* was obtained. It melted at 149–150°, and had  $[\alpha]_D^{25} + 54.5^\circ$  ( $p = 3.777$  in methyl alcohol). Its formula must be either



which is the true one, however, has not yet been determined. The *ammonium* salt of the monoamide was also prepared. Its specific rotation is  $+9.2^\circ$  ( $p = 4.694$  in methyl alcohol).

#### EXPERIMENTAL.

All rotations were measured with a Schmidt and Haensch half-shadow polarimeter. The instrument was not equipped with a thermostat, and hence it was impossible to measure rotations at a definite temperature. Densities were determined with a Mohr-Westphal balance, and therefore refer to water at 15°.

The tanacetone used in the following experiments was furnished by Schimmel & Co. It was purified before use by distillation under atmospheric pressure; the fraction boiling at 200–207° was then rectified once or twice under diminished pressure. The final product was a colourless oil of pleasant odour, with the following constants:

$$\text{b. p. } 81\text{--}82^\circ/11 \text{ mm.}; d_{42.15} = 0.924; [\alpha]_D^{25} + 67.4^\circ.$$

As a specimen of crude tanacetone, which had been kept for a long time in the laboratory, showed a specific rotation of about  $+30^\circ$ , it was deemed advisable to test the keeping qualities of the tanacetone used. A portion purified as above described was accordingly set aside, and its rotation examined from time to time. Its initial rotation was  $\alpha_D^{15} + 62.3^\circ$ , and after fifty-one weeks,  $\alpha_D^{15} + 60.1^\circ$ ; tanacetone therefore racemises with extreme slowness.

*Application of Grignard Reagent to Tanacetone and isoThujone.*

To ensure an excess of the Grignard reagent, 2 molecular proportions of magnesium and 2 of alkyl iodide were invariably used to one of the ketone. The reaction mixture was either poured on ice, acidified with acetic acid, and then extracted with ether, or, after pouring on ice, the whole was distilled in a current of steam, and the tertiary alcohol formed was extracted from the distillate by means of ether. The product of the treatment of tanacetone with magnesium methyl iodide was a yellow oil. This was distilled under atmospheric pressure, and the distillate well cooled in a freezing mixture. Partial solidification at once took place. The solid crystallised from methyl alcohol in white needles, melting at 84°:

0.2295 gave 0.6600 CO<sub>2</sub> and 0.2482 H<sub>2</sub>O. C=78.42; H=12.13.

C<sub>11</sub>H<sub>20</sub>O requires C=78.49; H=12.01 per cent.

*Rotatory power:*

$p = 4.058$  in ether;  $d_{15} = 0.728$ ;  $l = 2.2$  dcm.;  $\alpha_D = 1.93^\circ$ ;  $[\alpha]_D^{25} = 30.5^\circ$ .

$p = 4.191$  in methyl alcohol;  $d_{15} = 0.8055$ ;  $l = 2.2$  dcm.;  $\alpha_D = 1.93^\circ$ ;  
 $[\alpha]_D^{25} = 26.6^\circ$ .

The process of cooling and filtering was repeated until no more solid separated, and the remaining oil was distilled. The main fraction boiled at 204°. To make certain of the absence of unattacked tanacetone, the oil was treated several times with semicarbazide solution. Not a trace of semicarbazone was obtained after long keeping. Hence the absence of tanacetone is proved.

The results of analysis were in agreement with theory.

*Rotatory power:*

$p = 5.236$  in ether;  $d_{15} = 0.731$ ;  $l = 2.2$  dcm.;  $\alpha_D = 3.016^\circ$ ;  $[\alpha]_D^{25} = 35.9^\circ$ .

$p = 5.077$  in methyl alcohol;  $d_{15} = 0.8050$ ;  $l = 2.2$  dcm.;  $\alpha_D = 3.00^\circ$ ;  
 $[\alpha]_D^{25} = 33.4^\circ$ .

Curiously enough, neither the solid nor the liquid alcohol gives a urethane when treated with phenylcarbimide.

*Stability of the cycloPropane Ring in the Homothujyl Alcohols.*

One gram of solid homothujyl alcohol (m. p. 84°) was suspended in 500 c.c. of 5 per cent. sulphuric acid, and mechanically shaken daily for three weeks. The reaction mixture was then carefully neutralised with sodium hydroxide, and distilled in a current of steam for ten minutes in order to remove unattacked alcohol. The liquid in the distilling flask was then cooled and thoroughly extracted with ethyl acetate. After evaporation of the solvent, mere traces of an additive product were found.



Five grams of the liquid homothujyl alcohol, when treated in the same way with 1 litre of 5 per cent. sulphuric acid, gave a similar result.

*Preparation of  $\alpha$ -Thujaketonic Acid from Tanacetone.*

Seventy-five grams of crude tanacetone ( $n_D + 64^\circ$ ) were treated with the calculated amount (two atomic proportions of oxygen) of 5 per cent. permanganate solution, and the mixture was shaken mechanically until the permanganate was decolorised (two to three hours). The manganese oxide was then filtered off, and the filtrate evaporated on the water-bath until a skin began to form on the surface. If, before evaporating, oily drops (unattacked tanacetone or *l*-fenchone) were seen floating on the surface of the liquid, these were removed by means of a separating funnel. In order to prevent any harmful action of the alkali during the process of evaporation, small quantities of a solution of sulphurous acid were added from time to time, care being taken never to make the liquid acid in reaction. As soon as a skin began to form on the surface of the liquid, it was filtered, cooled, and acidified with dilute sulphuric acid. The  $\alpha$ -thujaketonic acid usually separated at once in solid form. On crystallisation from boiling water, it melted at  $75-76^\circ$ ; 75 grams of tanacetone gave 45 to 50 grams of  $\alpha$ -thujaketonic acid.

*Rotatory Power of  $\alpha$ -Thujaketonic Acid (m. p.  $75-76^\circ$ ).*

Solvent.	$p$ .	$d$ .	$l$ .	$\alpha_D$ .	$[\alpha]_D$ .
Ether.....	6.945	0.742 ( $14^\circ$ )	2.2 dm.	+22.00 ( $14^\circ$ )	+194.0 <sup>o</sup>
Glacial acetic acid..	4.8163	1.0524 (19)	1	10.386 (19)	224.1
Methyl alcohol.....	5.5649	0.8064 (19)	1	9.84 (19)	214.3
Chloroform .....	5.132	1.453 (18)	1	18.313 (18)	244.3
Water .....	0.6754	1.002 (13)	2.2	3.633 (18)	244.0

As the rotations of the oxime and semicarbazone of  $\alpha$ -thujaketonic acid have never hitherto been published, these compounds, together with its ammonium salt, were prepared and their rotations examined.

*Rotatory Power of Semicarbazone of  $\alpha$ -Thujaketonic Acid (m. p.  $183-184^\circ$ ).*

$p = 2.290$  in glac. acetic acid;  $d_{16} = 1.0605$ ;  $l = 2.2$  dm.;  $\alpha_D^{16} + 12.17^\circ$ ;  $[\alpha]_D^{16} + 227.8^\circ$ .

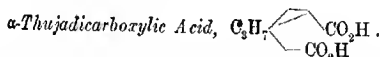
*Oxime of  $\alpha$ -Thujaketonic Acid.*—This compound was prepared in two different ways, namely, in alkaline and in neutral solution. The products obtained after recrystallisation from methyl alcohol differed both in melting point and in rotatory power. The oxime prepared in alkaline solution according to Lazell's method (*Dist.*,

(Göttingen, 1896, p. 26) melted at 169—170°, in good agreement with his result (169°), and had  $[\alpha]_D -5.00^\circ$  in methyl alcohol ( $p=3.933$ ).

The oxime prepared in neutral solution melted at 174—175°, and showed the following rotation values:  $p=4.473$  in methyl alcohol—no measurable rotation;  $p=1.7008$  in glacial acetic acid;  $d_{14}=1.058$ ;  $l=1$  dcm.;  $\alpha_D +0.10^\circ$ ;  $[\alpha]_D +5.56^\circ$ . In dilute sodium hydroxide solution the rotation was strongly negative. It was at first thought that these two oximes were stereoisomerides. Careful comparison has, however, since proved that this is not the case. By repeated crystallisation from methyl alcohol, the oxime of lower melting point is converted into the other, and a mixture of the two then melts unchanged at 174—175°.

*Rotatory Power of the Ammonium Salt of  $\alpha$ -Thujaketonic Acid.*

$p=0.881$  in water;  $d_{19}=1.007$ ;  $l=2.2$  dcm.;  $\alpha_D^{19} +3.333^\circ$ ;  $[\alpha]_D^{19} +170^\circ$ .



The  $\alpha$ -thujadicarboxylic acid used was prepared by the methods of both Semmler and Fromm (*loc. cit.*). The larger portion was, however, prepared by Semmler's method from  $\alpha$ -thujaketonic acid. It melted at 141—142°.

*Rotatory power:*

Solvent.	$p$ .	$d$ .	$l$ .	$\alpha_D$ .	$[\alpha]_D$ .
Ether .....	4.991	0.734 (15°)	2.2 dcm.	+8.47 (15°)	+105.1°
Glacial acetic acid ...	4.9177	1.0586 (18)	1 "	+6.933 (18)	133.2
Chloroform .....	2.8728	1.480 (15)	1 "	+7.29 (15)	171.5
Methyl alcohol .....	4.7043	0.810 (16)	1 "	+3.96 (16)	104.0
Water .....	0.7323	1.003 (18)	2.2 "	+2.183 (18)	135.1

*Rotatory Power of Ammonium Hydrogen Salt of  $\alpha$ -Thujadicarboxylic Acid.*

$p=0.793$  in water;  $d_{17}=1.005$ ;  $l=2.2$  dcm.;  $\alpha_D^{17} +0.266^\circ$ ;  $[\alpha]_D^{17} +15.2^\circ$ .

*Rotatory Power of Normal Ammonium Salt of  $\alpha$ -Thujadicarboxylic Acid.*

$p=3.805$  in water;  $d_{18}=1.0105$ ;  $l=2.2$  dcm.;  $\alpha_D^{18} -0.453^\circ$ ;  $[\alpha]_D^{18} -5.3^\circ$ .  
 $p=1.20$  in water;  $d=1.00$ ;  $l=2.2$  dcm.;  $\alpha_D -0.30^\circ$ ;  $[\alpha]_D -7.1^\circ$ .



This compound was first prepared by Semmler (*Ber.*, 1892, 25, 3349). Its rotation has not previously been published.

*Rotatory power:*

$p = 4.069$  in ether;  $d_{17} = 0.730$ ;  $l = 1$  dcm.;  $\alpha_D^{17} + 0.30^\circ$ ;  $[\alpha]_D^{17} + 10.1^\circ$ .  
 $p = 2.642$  in chloroform;  $d_{13} = 1.481$ ;  $l = 1$  dcm.;  $\alpha_D^{13} + 0.33^\circ$ ;  $[\alpha]_D^{13} + 8.43^\circ$ .

Heating with dilute hydrochloric acid converts the anhydride readily into the original acid.

*Preparation of the Monoamide of  $\alpha$ -Thujadicarboxylic Acid and its Ammonium Salt.*

Five grams of the pure anhydride of  $\alpha$ -thujadicarboxylic acid (m. p.  $56^\circ$ ), prepared as described by Semmler (*loc. cit.*), were dissolved in warm absolute alcohol, and the well-cooled solution saturated with dry ammonia gas. On keeping, a white solid slowly separated. This was dissolved in the least possible amount of water, and the solution rendered just acid with hydrochloric acid. Either at once or on keeping, fine white crystals separated, which were sparingly soluble in water, ether, or chloroform, readily so in alkalis. They were purified by redissolving in the least possible amount of dilute ammonia solution, and precipitating with hydrochloric acid. The substance melted at  $149$ – $150^\circ$ , or eight degrees higher than  $\alpha$ -thujadicarboxylic acid:

0.1796 gave 0.3844  $CO_2$  and 0.1313  $H_2O$ . C = 58.37; H = 8.209.

$C_9H_{15}O_3N$  requires C = 58.34; H = 8.167 per cent.

*Rotatory power in methyl alcohol:*

$p = 3.777$ ;  $d_{15} = 0.8084$ ;  $l = 1$  dcm.;  $\alpha_D^{15} + 1.666^\circ$ ;  $[\alpha]_D^{15} + 54.5^\circ$ .

Three hours later the rotatory power was unchanged.

The white solid which separated from the ammonia-alcoholic solution of the anhydride was recrystallised from absolute alcohol and analysed. It proved to be the ammonium salt of the monoamide:

0.1813 gave 0.3637  $CO_2$  and 0.1473  $H_2O$ . C = 54.71; H = 9.088.

$C_9H_{13}O_3N_2$  requires C = 53.42; H = 8.973 per cent.

The high result for carbon is satisfactorily accounted for by the presence of traces of the monoamide, doubtless formed by hydrolysis during the process of crystallisation.

*Rotatory power:*

$p = 1.713$  in water;  $d_{17} = 1.006$ ;  $l = 2.2$  dcm.;  $\alpha_D^{17} - 0.666^\circ$ ;  
 $[\alpha]_D^{17} - 17.6^\circ$ .  
 $p = 4.694$  in methyl alcohol;  $d_{18} = 0.808$ ;  $l = 1$  dcm.;  $\alpha_D^{18} + 0.35^\circ$ ;  
 $[\alpha]_D^{18} + 9.2^\circ$ .

*Stability of the cycloPropane Ring in  $\alpha$ -Thujaktonic Acid.*

Ten grams of  $\alpha$ -thujaktonic acid were dissolved in 1000 c.c. of 20 per cent. hydrochloric acid, and boiled for two hours. Steam was then passed into the mixture for fifteen minutes, and an oil distilled over which proved to be an unsaturated hydrocarbon identical in odour with dihydro- $\psi$ -cumene. When rectified over sodium, it boiled at  $160-165^\circ$  (dihydro- $\psi$ -cumene boils at  $160^\circ$ ). An attempt to characterise it more nearly by preparation of the crystalline trinitrodihydro- $\psi$ -cumene failed. From the residues in the distilling flask, a large quantity of an inactive acid oil was obtained. All attempts to crystallise this oil failed.

*Stability of the cycloPropane Ring in  $\alpha$ -Thujadicarboxylic Acid.*

One gram of the acid was boiled for two hours with 20 per cent. hydrochloric acid, and the substance then recovered by evaporation on the water-bath. It melted at  $141-142^\circ$  (unchanged), and had  $[\alpha]_D$  ( $p = 2.703$  in ether)  $+109^\circ$  [the pure substance has  $[\alpha]_D$  ( $p = 4.991$  in ether)  $+105^\circ$ ].

One gram of the acid, boiled for one and a-half hours with 10 per cent. sodium hydroxide solution, gave a similar result.

*Esterification of  $\alpha$ -Thujadicarboxylic Acid.*

The esterification was carried out in the usual way by saturating the alcoholic solution of the acid with hydrogen chloride.

*Dimethyl Ester,  $C_7H_{12}(CO_2Me)_2$ .*

B. p.  $126-127^\circ/13$  mm.; under the ordinary pressure  $244-247^\circ$ ;  $d_m = 1.0535$ ;  $n_D = 1.4506$ . When boiled for two hours with aniline under reflux, it does not give an anilide. It reacts with metallic sodium in ethereal solution, giving a sodio-derivative:

$0.2153$  gave  $0.4853$   $CO_2$  and  $0.1684$   $H_2O$ .  $C = 61.47$ ;  $H = 8.756$ .

$C_{11}H_{18}O_4$  requires  $C = 61.65$ ;  $H = 8.472$  per cent.

*Rotatory power:*

$\alpha_D^{18} = 1.054$ ;  $l = 1$  dcm.;  $\alpha_D^{18} + 150.18^\circ$ ;  $[\alpha]_D^{18} + 142.5^\circ$ .

A month later unchanged.

$n_D = 4.746$  in ether;  $d_{20} = 0.731$ ;  $l = 1$  dcm.;  $\alpha_D^{20} + 4.933^\circ$ ;  $[\alpha]_D^{20} + 142.1^\circ$ .  
 $n_D = 10.86$  in ether;  $d_{20} = 0.7465$ ;  $l = 1$  dcm.;  $\alpha_D^{20} + 11.65^\circ$ ;  $[\alpha]_D^{20} + 139.2^\circ$ .

*Diethyl Ester,  $C_7H_{12}(CO_2Et)_2$ .*

B. p.  $138-140^\circ/12-13$  mm.;  $d_{19} = 1.019$ :

0.2064 gave 0.4861  $CO_2$  and 0.1690  $H_2O$ . C = 64.23; H = 9.163.

$C_{18}H_{22}O_4$  requires C = 64.42; H = 9.157 per cent.

*Rotatory power:*

$d_{19} = 1.019$ ;  $l = 1$  dcm.;  $\alpha_D^{19} + 116.27^\circ$ ;  $[\alpha]_D^{19} + 114.1^\circ$ .

Four and a-half months later,  $[\alpha]_D + 114.3^\circ$ .

$n_D = 5.135$  in ether;  $d_{18} = 0.731$ ;  $l = 1$  dcm.;  $\alpha_D^{18} + 4.35^\circ$ ;  $[\alpha]_D^{18} + 115.9^\circ$ .

$n_D = 10.073$  in ether;  $d_{18} = 0.7437$ ;  $l = 1$  dcm.;  $\alpha_D^{18} + 7.93^\circ$ ;  $[\alpha]_D^{18} + 106^\circ$ .

*Di-n-propyl Ester,  $C_7H_{12}(CO_2Pr^a)_2$ .*

B. p.  $157-160^\circ/11-13$  mm.;  $d_{16.16} = 0.9969$ :

0.1664 gave 0.4039  $CO_2$  and 0.1531  $H_2O$ . C = 66.20; H = 10.29.

$C_{15}H_{20}O_4$  requires C = 66.61; H = 9.699 per cent.

*Rotatory power:*

$d_{12} = 0.9973$ ;  $l = 1$  dcm.;  $\alpha_D^{12} + 84.5^\circ$ ;  $[\alpha]_D^{12} + 84.7^\circ$ .

$n_D = 6.786$  in ether;  $d_{17} = 0.740$ ;  $l = 1$  dcm.;  $\alpha_D^{17} + 4.28^\circ$ ;  $[\alpha]_D^{17} + 85.2^\circ$ .

*Diisobutyl Ester,  $C_7H_{12}(CO_2C_4H_9)_2$ .*

B. p.  $174-176^\circ/12-14$  mm.;  $d_{15} = 0.9908$ .

0.1725 gave 0.4258  $CO_2$  and 0.1502  $H_2O$ . C = 67.32; H = 9.74.

$C_{17}H_{20}O_4$  requires C = 68.45; H = 10.14 per cent.

*Rotatory power:*

$d_{12} = 0.991$ ;  $l = 1$  dcm.;  $\alpha_D^{12} + 76.92^\circ$ ;  $[\alpha]_D^{12} + 77.62^\circ$ .

$n_D = 5.577$  in ether;  $d_{12} = 0.7385$ ;  $l = 1$  dcm.;  $\alpha_D^{12} + 2.95^\circ$ ;  $[\alpha]_D^{12} + 71.6^\circ$ .

$n_D = 13.709$  in ether;  $d_{12} = 0.7610$ ;  $l = 1$  dcm.;  $\alpha_D^{12} + 7.616^\circ$ ;  $[\alpha]_D^{12} + 73.0^\circ$ .

*Diisoamyl Ester,  $C_7H_{12}(CO_2C_5H_{11})_2$ .*

(The amyl alcohol used had  $n_D - 1.1^\circ$  in a 1-dcm. tube.)

B. p.  $187-190^\circ/10-12$  mm.;  $d_{15} = 0.9934$ :

0.2048 gave 0.5066  $CO_2$  and 0.1812  $H_2O$ . C = 67.46; H = 9.897.

$C_{19}H_{24}O_4$  requires C = 69.88; H = 10.50 per cent.

*Rotatory power:*

$d_{15} = 0.9934$ ;  $l = 1$  dcm.;  $\alpha_D^{15} + 72.95^\circ$ ;  $[\alpha]_D^{15} + 73.5^\circ$ .

$n_D = 4.4314$  in ether;  $d_{16} = 0.730$ ;  $l = 1$  dcm.;  $\alpha_D^{16} + 2.366^\circ$ ;  $[\alpha]_D^{16} + 73.1^\circ$ .

*Monobenzyl Ester*,  $\text{CO}_2\text{H}\cdot\text{C}_7\text{H}_{13}\cdot\text{CO}_2\cdot\text{C}_7\text{H}_7$ .

B. p. 215—220°/12—14 mm.

0.2311 gave 0.5931  $\text{CO}_2$  and 0.1492  $\text{H}_2\text{O}$ . C = 69.99; H = 7.22. $\text{C}_{16}\text{H}_{20}\text{O}_4$  requires C = 69.52; H = 7.30 per cent.*Rotatory power*: $\alpha_D^{25} = +5.66$  in ether;  $d_{17}^{25} = 0.735$ ;  $l = 1$  dm.;  $\alpha_D^{25} = +1.166^\circ$ ;  $[\alpha]_D^{25} = +34.7^\circ$ .*Decomposition Products of the Sodio-derivative of the Dimethyl (or Diethyl) Ester of α-Thujadicarboxylic Acid.*

On warming the sodio-derivative of the dimethyl ester with water, the odour of tanacetophorone was observed. In order to study this change, about 20 grams of ester were treated with metallic sodium, and the product distilled in a current of steam. The distillate, when treated with semicarbazide solution, gave at once a semicarbazone. This was carefully compared with the semicarbazone prepared from some tanacetophorone kindly furnished by Prof. Wallach, and their identity established. Both semicarbazones crystallise from methyl alcohol in shining leaflets, melting and decomposing at 187—188°. A mixture of the two semicarbazones behaves in the same way. The results of analysis were also in good agreement with theory:

0.1732 gave 0.3777  $\text{CO}_2$  and 0.1287  $\text{H}_2\text{O}$ . C = 59.47; H = 8.31. $\text{C}_9\text{H}_{15}\text{ON}_3$  requires C = 59.62; H = 8.35 per cent.

The semicarbazone was decomposed with oxalic acid and the tanacetophorone recovered. It showed the following constants: b. p. 215—217°; 99°/17—18 mm.;  $d_{19/15}^{20} = 0.9453$  (Semmler, *Ber.*, 1892, 25, 3350, gives the following constants for tanacetophorone: b. p. 212—214°; 89—90°/13 mm.;  $d_{20}^{20} = 0.9378$ ).

The cooled residue remaining in the distillation flask was extracted with ether; the acid oil obtained in this way was dissolved in boiling water. After some time two acids slowly crystallised. These were mechanically separated and examined. Both were inactive. One melted at 116—117°, and was identical with β-thujadicarboxylic acid; the other melted at 150—151°. This was analysed:


0.1171 gave 0.2492  $\text{CO}_2$  and 0.0810  $\text{H}_2\text{O}$ . C = 58.04; H = 7.73. $\text{C}_9\text{H}_{14}\text{O}_4$  requires C = 58.03; H = 7.58 per cent.

The silver salt was prepared:


0.1172 gave 0.0634 Ag. Ag = 54.09.

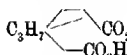
 $\text{C}_9\text{H}_{12}\text{O}_4\text{Ag}_2$  requires Ag = 53.97 per cent.

*Summary.*


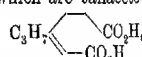
Tanacetone ( $\beta$ -thujone), when treated with magnesium methyl iodide, yields two tertiary homothujyl alcohols,  $C_8H_{17}$  ,

one a solid, m. p.  $84^\circ$ ,  $[\alpha]_D -30.5^\circ$ ; the other, a liquid, b. p.  $204^\circ$ ,  $[\alpha]_D +35^\circ$ . In both these alcohols, as in thujyl alcohol, the cyclopropane ring is stable towards cold 5 per cent. sulphuric acid. The three next higher homologues of homothujyl alcohol are liquids. *iso*Thujone, when treated with magnesium methyl iodide in the same way, does not yield a solid tertiary alcohol.

$\alpha$ -Thujaketonic acid,  $C_8H_{15}$  , is decomposed by boiling with 20 per cent. hydrochloric acid with the formation of an unsaturated hydrocarbon (b. p.  $160-165^\circ$ ), probably dihydro- $\psi$ -cumene.

$\alpha$ -Thujadicarboxylic acid,  $C_8H_{15}$  , prepared from  $\alpha$ -thujaketonic acid by oxidation, is quite stable towards boiling 20 per cent. hydrochloric acid and boiling 10 per cent. sodium hydroxide.

$\alpha$ -Thujadicarboxylic acid can be easily esterified in the ordinary way. *Dimethyl*, *diethyl*, *di-n-propyl*, *diisobutyl*, and *diisooamyl* esters have been prepared. All are colourless, odourless liquids.

The dimethyl and diethyl esters of  $\alpha$ -thujadicarboxylic acid give a sodio-derivative, the decomposition products of which are tanacetophorone,  $C_8H_{17}$  ,  $\beta$ -thujadicarboxylic acid,  $C_8H_{17}$  , and an unknown inactive dicarboxylic acid,  $C_9H_{11}O_4$ , melting at  $150-151^\circ$ .

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CXL.—*Optically Active Methoxysuccinic Acid from Malic Acid.*By THOMAS PURDIE, F.R.S., and GEORGE BALLINGALL NEAVE,  
M.A., D.Sc.

OPTICALLY active monoalkyloxysuccinic acids were obtained a number of years ago (Trans., 1893, 63, 217, and succeeding papers) by the resolution of the corresponding inactive acids with the aid of alkaloids. The inactive acids were prepared from fumaric esters, which possess the property of combining with the elements of alcohols under the action of sodium alkyl oxides.

Later, in the course of our first experiments on alkylation by means of dry silver oxide and alkyl iodides (Trans., 1899, 75, 157), it was shown that ethyl *l*-ethoxysuccinate could be prepared from ethyl malate. The yield of the pure ester, however, was unsatisfactory, as the product contained much unaltered malate, which was removed by treating the mixture with cold potassium hydroxide solution. This process naturally results in a diminished yield of alkylated product, as compared with the method of repeated alkylation which is now adopted. We have now employed the method referred to for the preparation of the methyl, ethyl, and propyl esters of *l*-methoxysuccinic acid with the view of controlling and extending the polarimetric observations made formerly (*loc. cit.*) on the compounds obtained by resolution of the inactive acid.

We find that the esters of *l*-methoxysuccinic acid are easily obtained in the pure state by methylating the corresponding malic esters, provided that a sufficient excess of the alkylating agent is used. Some oxidation occurs in the course of the action, but the oxidation products are readily removed by subsequent fractional distillation. In preparing methyl *l*-methoxysuccinate, dry silver oxide (2 mols.) was added in small quantities at a time to a mixture of methyl malate (1 mol.) and methyl iodide (4 mols.), and after all the oxide had been added and spontaneous action had ceased, the mixture was heated for two hours on a water-bath. The liquid product was extracted from the silver residues by means of ether, and after being dried with sodium sulphate and freed from ether, was fractionated under diminished pressure. Twenty-five grams of methyl malate ( $\alpha_D^{20} - 8.36^\circ$ ;  $l=1$ ) gave, after the first distillation, 22 grams of the methylated ester boiling at  $113-114^\circ/15$  mm., and showing the observed rotation  $\alpha_D^{20} - 61.74^\circ$  ( $l=1$ ). After three more distillations, the rotation was constant at  $-62.79^\circ$ , and was not altered by repeating the methylation.



The active methyl methoxysuccinate, formerly prepared by resolution of the inactive acid (Trans., 1895, 67, 970), was the ester of the *d*-acid. The antipodal forms are liquid, and could not be solidified by cooling. The inactive ester obtained from methyl fumarate (Trans., 1891, 59, 469), on the other hand, is crystalline, and melts at 28°. On mixing equal weights of the two oppositely active esters derived as above described from different sources and cooling the mixture to 0°, crystallisation did not occur spontaneously, but on adding a nucleus of the inactive form the whole mass quickly solidified. After being again melted, the mixture solidified spontaneously at the ordinary temperature, and now melted at the same temperature as the inactive substance, 28°.

*Ethyl l-methoxysuccinate* was prepared from ethyl malate ( $\alpha_{D^{20}} - 11.76^\circ$ ,  $l=1$ ) in the same manner as the methyl ester. The *propyl* ester was prepared by the action of propyl iodide on the silver salt obtained from methyl *l*-methoxysuccinate. The results of analysis and the polarimetric and other observations made on the liquid esters are recorded below.

*Methyl l-methoxysuccinate*, h. p. 113—114°/15 mm.:

Found, C=47.46; H=7.08.

$C_5H_{10}O_5$  requires C=47.73; H=6.82 per cent.

*Ethyl l-methoxysuccinate*, h. p. 126°/17 mm.:

Found, C=52.88; H=7.84.

$C_7H_{14}O_5$  requires C=52.94; H=7.84 per cent.

*Propyl l-methoxysuccinate*, h. p. 145—146°/12 mm. The *silver* salt obtained from the product of hydrolysis of methyl *l*-methoxysuccinate, which was used in preparing this ester, gave:

Found, C=16.45; H=1.90; Ag=59.58.

$C_5H_9O_5Ag_2$  requires C=16.58; H=1.66; Ag=59.65 per cent.

The observations from which the molecular rotations, recorded below, are calculated were taken in a 1-dm. tube.

#### *l*-Methoxysuccinic Esters (Pure Liquids).

	$d\ 20^\circ/4^\circ$	$[M]_D^{20^\circ}$	$d\ 40^\circ/4^\circ$	$[M]_D^{40^\circ}$	$d\ 60^\circ/4^\circ$	$[M]_D^{60^\circ}$	$c^*[a]_{20-60^\circ}$
Methyl...	1.1415	-96.8*	1.1199	-95.6*	1.0983	-93.9*	-0.0008
Ethyl ...	1.0676	102.9	1.0476	101.5	1.0273	100.1	-0.0007
Propyl ...	1.0312	109.0	1.0101	107.3	0.9908	105.6	-0.0008

\* Temperature-coefficient, as defined by Walden (Ber., 1905, 38, 363).

The polarimetric observations on solutions of the three esters, from which the molecular rotations recorded in the following tables are calculated, were taken in a 2-dm. tube at 20°. The concentrations by volume ( $c$ ) were determined from the specific gravities of the solutions ( $d\ 20^\circ/4^\circ$ ) and the concentrations by weight. The specific gravities ( $d\ 20^\circ/4^\circ$ ) of the benzene and ethyl

alcohol used in the case of the methyl and ethyl esters were 0.8785 and 0.7912 respectively; those of the solvents used in the case of the propyl ester were 0.8789 and 0.7910 respectively. The molecular solution volumes (M.S.V.) were calculated by the usual formula.

*Methyl l-Methoxysuccinate.*

$[M]_D^{20} - 96.8^\circ$ ,  $d\ 20^\circ/4^\circ\ 1.1415$ ,  $M/d\ 154.2$ .

Solvent.	$c$ .	$d\ 20^\circ/4^\circ$ .	$[M]_D^{20}$ .	M.S.V.
Benzene .....	19.9734	0.9238	-114.7*	154.9
	10.0175	0.9012	118.1	154.9
	5.0399	0.8899	120.0	155.0
Ethyl alcohol ...	20.0056	0.8593	-90.6	153.4
	10.0456	0.8225	90.2	153.1
	5.0038	0.8070	91.1	152.2

*Ethyl l-Methoxysuccinate.*

$[M]_D^{20} - 102.9^\circ$ ,  $d\ 20^\circ/4^\circ\ 1.0676$ ,  $M/d\ 191.1$ .

Solvent.	$c$ .	$d\ 20^\circ/4^\circ$ .	$[M]_D^{20}$ .	M.S.V.
Benzene .....	20.0429	0.9138	-118.2*	191.3
	10.0090	0.8962	120.4	191.1
	5.0339	0.8872	123.4	192.1
Ethyl alcohol...	19.9254	0.8434	-96.2	190.3
	9.9748	0.8174	97.3	190.1
	5.0263	0.8045	97.6	189.6

*Propyl l-Methoxysuccinate.*

$[M]_D^{20} - 109.0^\circ$ ,  $d\ 20^\circ/4^\circ\ 1.0312$ ,  $M/d\ 225.0$ .

Solvent.	$c$ .	$d\ 20^\circ/4^\circ$ .	$[M]_D^{20}$ .	M.S.V.
Benzene .....	19.9105	0.9082	-122.3*	225.1
	10.0140	0.8935	125.7	225.5
	4.9880	0.8865	126.7	223.7
Ethyl alcohol ...	19.8346	0.8376	-101.1	224.4
	10.0320	0.8149	101.1	223.4
	6.0014	0.8054	100.1	222.9

The optically active diamide and dianilide of methoxysuccinic acid, which have not been hitherto examined, were readily obtained from methyl *l*-methoxysuccinate by the action of methyl-alcoholic ammonia solution at the ordinary temperature, and of aniline at  $130-140^\circ$  respectively. The analysis of these compounds and the results of polarimetric observations ( $l=2$ ) made on their solutions are recorded below. The molecular rotations of maldiamide and maldianilide are appended for comparison.

*l*-Methoxysuccindiamide crystallises from methyl-alcoholic solu-

tion in prisms melting at 178—179°. The inactive amide melts at 175° (Trans., 1891, 59, 471):

Found, C=41.13; H=7.01; N=19.33.

$C_8H_{10}O_3N_2$  requires C=41.10; H=6.85; N=19.18 per cent.

*l*-Methoxysuccindianilide crystallises from hot benzene solution in small needles, melting at 158—159°:

Found, N=9.58.

$C_{17}H_{15}O_3N_2$  requires N=9.40 per cent.

Solvent.	<i>l</i> -Methoxy-succindianilide.			<i>l</i> -Methoxy-succindianilide.		
	<i>c</i> .	$[M]_D^{20}$ .	Maldi-amide, $[M]_D^{20}$ .	<i>c</i> .	$[M]_D^{20}$ .	Maldi-amide, $[M]_D^{20}$ .
Water .....	7.4860	-59.4°	-50.2°*	—	—	—
.....	1.2165	58.8	—	—	—	—
Methyl alcohol .....	1.0460	83.0	—	2.1096	-231.7°	—
Acetic acid .....	3.9954	60.8	59.7 †	2.1193	158.9	-172.3°
.....	2.9833	60.7	—	1.5408	158.6	—
Pyridine .....	0.2740	117.2	76.2 †	2.4546	197.9	287.1 ‡
.....	—	—	—	1.2063	196.4	—

\* Walden, *Zeitsch. physikal. Chem.*, 1895, 17, 265.

† McCrae, Trans., 1893, 83, 1326.

‡ Guye and Babel, *Arch. Sci. phys. nat.*, 1899, [iv], 7, 23.

The observation on methoxysuccindianilide in methyl-alcoholic solution was made at 16°. Methoxysuccindiamide being very sparingly soluble in pyridine, the rotation given for it in this solvent is only approximate.

#### Discussion of Results.

Considering the uncertainty of obtaining active compounds displaying the maximum rotation by the methods of resolution, the rotatory powers of the esters formerly obtained from *dl*-methoxysuccinic acid are in fair agreement with the more exact values now found for the same compounds obtained from malic acid. It was stated (Trans., 1895, 67, 979) that the value there recorded for methyl *d*-methoxysuccinate was probably about 2° low, and that the actual value should therefore be about  $[\alpha]_D^{25} + 54.5^\circ$ . The value now found for the *l*-ester from malic acid, corrected for temperature, is  $[\alpha]_D^{25} - 55.27^\circ$ . The values for the ethyl *l*-ester from the two different sources are  $[\alpha]_D^{18} - 50.11^\circ$  and  $-50.51^\circ$  respectively, and for the propyl *l*-ester,  $[\alpha]_D^{15} - 45.21^\circ$  and  $-47.19^\circ$ . The *l*-methoxysuccinic acid, now obtained by hydrolysing the methyl *l*-ester from methyl malate, gave in aqueous solution for  $c=6.135$ ,  $[\alpha]_D^{25} - 33.56^\circ$ ; the *d*-acid from the alternative source (Trans., 1893, 63, 224) in approximately the same concentration gave  $[\alpha]_D^{18} + 33.04^\circ$ .

The optical relationships of the methyl, ethyl, and propyl *l*-mono-methoxysuccinates resemble those of the corresponding *d*-dimethoxy

succinates already described (Purdie and Irvine, *Trans.*, 1901, **79**, 963), and a general parallelism is observable in the relationships of each series to the parent malic and tartaric series. We tabulate below the molecular rotations of the four series of liquid esters. Observations at 20° being impossible in the case of methyl *d*-dimethoxysuccinate (m. p. 53°), values at 60° are given for all the methoxysuccinates; the values of the tartrates and dimethoxy-derivatives have been halved, so as to exhibit the optical effect of only one of the two asymmetric groups. The intermediate columns show the differences between the molecular rotations of the methylated esters and the corresponding malates (Walden, *loc. cit.*) and tartrates (Pictet, *Jahresber.*, 1882, 856):

	<i>l</i> -Monomethoxy- succinates.			<i>d</i> -Dimethoxy- succinates.			Tartrates.
	[M] <sub>D</sub> <sup>60</sup> .	Diff.	Malates. [M] <sub>D</sub> <sup>60</sup> .	[M] <sub>D</sub> <sup>60</sup> /2.	Diff.	[M] <sub>D</sub> <sup>60</sup> /2.	
Methyl ...	-93.9°	82.8°	-11.1°	+85.0°	83.1°	+1.91°	
Ethyl ...	100.1	80.3	19.3	99.9	92.0	7.99	
Propyl ...	105.6	80.4	25.3	106.3	91.8	14.55	

It is seen from the tabulated figures that the methylation of malic and tartaric esters produces a remarkable increase of rotatory power in the *lævo*- and *dextro*-sense respectively. The alkyl radicles when introduced into these esters have, in fact, a much greater effect in the directions indicated than any of the acyl groups. It has been previously pointed out (Purdie and Irvine, *loc. cit.*) that, regarding the malic esters as derived from *d*-malic acid, the radicles in respect of their optical influence as substituents in the cases under consideration may be said to stand at the positive, the aromatic acyl groups at the negative, end of the scale, whilst the aliphatic acyl groups hold an intermediate position.

The *etbereal* mono- and di-methoxysuccinates, like the parent malates and tartrates, exhibit an increase of rotatory power with ascent of the series. Inspection of the columns of differences shows that the optical effect of methylating the three malates is remarkably constant, raising the rotation of each by about the same amount (80° to 83°). The rise produced in the case of ethyl and propyl tartrates is also uniform, although considerably greater (about 92°), the result being that despite the lower activity of the tartrates\* as compared with the malates, ethyl and propyl dimethoxysuccinates show nearly the same values as the corresponding monomethoxy-esters. The optical effect of methylating methyl tartrate, however, diverges considerably from the regularity exhibited by the other malates and tartrates. The molecular rotation of methyl dimethoxysuccinate is about 9° short of that of methyl monomethoxy-

\* As stated above, the halved molecular rotations of the tartrates and the dimethoxy-derivatives are here referred to.

succinate, the increase of rotation produced by the methylation of methyl tartrate being only  $83.1^\circ$ . This exceptional result may be related to the fact that, whilst methyl monomethoxysuccinate is liquid even at  $0^\circ$ , the dimethoxysuccinate at the temperature of observation ( $60^\circ$ ) is but little removed from its melting point, and is therefore possibly in a state of abnormal aggregation.

The rotatory powers of the mono- and di-methoxysuccinic esters are similarly influenced by (1) change of temperature, (2) solvents, (3) concentration in solutions. Certain regularities with respect to the influence of these factors are also observable in comparing malates and tartrates with the mono- and di-methylated esters respectively, but the relationships here become extremely complex, and require more extended investigation for their elucidation. With some exceptions, the optical effect of the three factors on the methoxy-esters is in the opposite sense to their effect on the parent hydroxy-esters.

With rise of temperature, within the limits of our observations, the mono- and di-methoxysuccinates examined show a diminution, the corresponding malates and tartrates, like lactates and glycerates (Walden, *Ber.*, 1905, 38, 364), an increase of rotatory power. The temperature-coefficients (p. 1518) of the three monomethoxy-esters have nearly the same value ( $-0.0008$ ), and those of the ethyl and propyl dimethoxy-esters ( $-0.0014$  and  $-0.0012$ ) do not differ very greatly from them. It is noteworthy that the abnormal sensitiveness to temperature which characterises the tartaric esters (Walden, *loc. cit.*) disappears when they are methylated.

All the three esters of the mono- and di-methoxysuccinic series (Trans., 1901, 79, 973) show a marked rise in the value of  $[M]_D^{20}$  when dissolved in benzene ( $c=20$  per cent.). A further rise occurs on dilution ( $c=5$  per cent.). A fall in value, much less in amount, is produced by solution of the monomethoxysuccinates in ethyl alcohol, and the same result holds for solution of the methyl and ethyl dimethoxysuccinates in methyl alcohol. The relationships of the dimethoxysuccinates with the tartrates in respect of the influence of solvents on their rotatory powers have been previously described (*loc. cit.*). With regard to the monomethoxysuccinates and the parent malates, the effects of benzene and of methyl alcohol on methyl and ethyl malates (Walden, *Ber.*, 1906, 39, 671) are again in the opposite sense to their effects on the corresponding methylated esters.

The well-known researches of Patterson have shown that in many instances a correspondence can be traced between changes of rotation and of molecular solution volume. Our observations on the three ethereal *l*-methoxysuccinates exhibit some regularities in

this connexion, which may be recorded. The increase of molecular rotation produced by solution of the esters in benzene is attended by a parallel increase of molecular volume. The initial increments of molecular rotation on dissolving the compounds in benzene ( $c=20$  per cent.) are  $17.9^\circ$ ,  $15.3^\circ$ , and  $13.3^\circ$  for the methyl, ethyl, and propyl terms respectively. The corresponding increments of molecular volume (0.7, 0.2, and 0.1) are small, but obviously diminish, like the increments of rotation, with ascent of the series. The further increase of rotation which occurs on diluting the benzene solutions is associated with a further slight increase of molecular solution volume. The molecular solution volume of the propyl ester, however, shows a maximum at the concentration  $c=10$  per cent., and a corresponding maximum of rotation might be expected at this point. Although no such maximum occurs, the smaller increase of rotation exhibited by this ester in the most dilute solution, when compared with the corresponding increases shown by the methyl and ethyl esters, indicates that its rotations are more nearly approaching a maximum.

As already stated, the initial effect of ethyl alcohol, in contradistinction to that of benzene, is a diminution of rotation; the effect of alcohol on molecular volume is also in the opposite sense to that of benzene. The changes which occur on diluting the alcoholic solutions do not show, however, any obvious connection between rotation and molecular solution volume.

The rotatory powers of malamide and tartramide and their derivatives have been systematically investigated by Frankland and his pupils in recent years (Trans., 1906, **89**, 1859; 1910, **97**, 154, and preceding papers). In both the malic and tartaric series, the aromatic amides show a much higher molecular rotation than the unsubstituted amides and alkylamides. Our observations on *l*-methoxysuccinamide and anilide in methyl alcohol and glacial acetic acid solutions (p. 1520) show that here also a great increase attends the introduction of a phenyl group into the simple amide.

A general similarity also prevails with respect to the influence of different solvents on the rotatory powers of maldiamide and maldianilide on the one hand, and of the corresponding methoxyderivatives on the other. Disregarding the effect of methyl alcohol, for which in the case of malamide no data are available, the values of both the diamides are at their lowest in water, and at their highest in pyridine solution. The rotations of both anilides are much higher in pyridine than in acetic acid solution.

It is particularly worthy of notice that the replacement of the group  $\text{CH}\cdot\text{OH}$  by  $\text{CH}\cdot\text{OMe}$ , which so largely enhances the rotatory power in the case of malic acid and its esters, has not the similar

effect in the case of the amide and anilide of malic acid, which was to be expected. The rotation of *l*-methoxysuccinamide, it is true, exceeds that of malamide in pyridine solution, and by a relatively small amount also in water solution, but the rotations of the methoxy-amide and anilide in the other solvents are either about equal to those of the corresponding unsubstituted malic compounds, or distinctly lower.

The metallic salts are the only other derivatives of malic acid, so far known, whose rotation is lowered by the alkylation of the alcoholic hydroxyl group.

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### CXLI.—*Optically Active Derivatives of l-Methoxy- and d-Dimethoxy-succinic Acids.*

By THOMAS PURDIE, F.R.S., and CHARLES ROBERT YOUNG, B.Sc.

IN continuation of previous work (see p. 1517 and Trans., 1901, 79, 957), we have prepared a number of derivatives of optically active mono- and di-methoxysuccinic acids, an account of which is contained in the following paper.

In view of the superior stability of the alkyloxy-group as compared with the hydroxyl group, it appeared probable that derivatives, such as acid chlorides and anhydrides, which cannot be obtained from malic or tartaric acids, could be prepared from the corresponding alkyloxy-acids. Derivatives of this nature should prove useful in the synthesis of optically active substances, and also for comparing the optical relationships of compounds of the succinic acid type.

We find that the methoxyl groups are, in general, not affected by the reagents used, and that the products are optically active, the only cases exceptional in this respect being the action of sodium methoxide and of magnesium phenyl bromide on methyl *l*-methoxy-succinate.

The chlorides and anhydrides of the mono- and di-methoxy-succinic acids are readily obtained from the corresponding acids by the action of phosphorus pentachloride and acetyl chloride respectively. The monomethoxy-compounds are both liquids which distill without decomposition; the dimethoxy-compounds are crystalline.

The constitution of succinyl chloride has been the subject of much discussion. In certain well-defined cases the compound reacts in the lactonic form; recently Meyer and Marx have shown conclusively (*Ber.*, 1908, 41, 2459) that with alcohols, on the other hand, it acts as if it had the ordinary constitution of an acid chloride. The substance is therefore tautomeric, but there is no satisfactory evidence to show whether it consists of one only of the two desmotropic forms or of a mixture of both.

We have not yet applied the reactions to mono- and dimethoxysuccinyl chlorides, which on the analogy of succinyl chloride should give derivatives of the lactonic type. We find, however, that with alcohols they react like succinyl chloride in the ordinary symmetric form. A specimen of the liquid methyl *l*-methoxysuccinate, obtained by interaction of the chloride and methyl alcohol, was practically identical in rotatory power with the ester prepared from the silver salt of the acid (*Trans.*, 1895, 67, 970), and also with that obtained by the methylation of methyl malate. Similarly, the crystalline methyl *d*-dimethoxysuccinate obtained from the corresponding acid chloride was identical in melting point and rotatory power with the product of methylation of methyl tartrate.

Moreover, we find that the polarimetric examination of solutions of these chlorides in indifferent solvents shows that the compounds exist in one form only, judging from the fact that the rotatory powers remain permanent under conditions which usually promote tautomeric change. Thus, a benzene solution of *l*-methoxysuccinyl chloride showed no mutarotation after forty-eight hours. The rotation of a similar solution of *d*-dimethoxysuccinyl chloride, to which a trace of aluminium chloride\* was added as a catalytic agent, remained unchanged after the lapse of six weeks. In another experiment a fresh quantity of the crystalline chloride was heated in a sealed tube at 100° for six hours in the fused state. This treatment produced no change in the melting point of the solidified substance or in its rotatory power in benzene solution, and no mutarotation occurred on addition of a trace of aluminium chloride and on prolonged keeping. The same observations were made on the compound immediately after being distilled, with the same negative results. We conclude from these experiments that, whatever be the case with succinyl chloride, its methoxy-derivatives are not mixtures of dynamic isomerides.

The methyl hydrogen esters of *l*-mono- and *d*-dimethoxysuccinic acids were readily obtained from the respective anhydrides by heating these with methyl alcohol. Both compounds are crystalline.

\* Aluminium chloride was used as, with this reagent and benzene, succinyl chloride is known to react in the lactonic form.

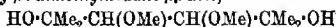


By passing dry ammonia gas into L-methoxysuccinic anhydride at 100°, a mixture of the amic acid and its ammonium salt was produced, from which the former was isolated by fractional crystallisation. The dry distillation of the amic acid gave a crystalline substance (melting point 59–61°), which analysis showed to have the composition of the imide, but lack of material prevented further examination.

The action of alcoholic sodium methoxide on methyl L-methoxysuccinate was undertaken in the hope of obtaining an optically active dimethoxysuccinylsuccinic ester. Condensation occurred, but the reaction was more complex than in the case of the unsubstituted succinic ester, one at least of the etheric methoxyl groups of the two condensing molecules being lost and the optical activity destroyed. The only product isolated was a pale yellow, amorphous solid, which in alcoholic solution gave a plum coloration with ferric chloride, changing to reddish-purple on dilution. It could not be crystallised, nor could crystalline derivatives be obtained from it. Combustion and estimation of methoxyl agreed with figures calculated for a closed-ring condensation of two molecules of methyl methoxysuccinate with the loss of three molecules of methyl alcohol, or for the isomeric substance which would result from an open-chain condensation of two molecules of methyl fumarate by the abstraction of one molecule of methyl alcohol. In general properties and in composition, it was identical with a condensation product previously obtained (Trans., 1891, 59, 472) from the action of alcoholic sodium methoxide on methyl fumarate. The substance appears to be of some interest, and will be examined later.

Valeur (*Compt. rend.*, 1901, 132, 833; *Bull. Soc. chim.*, 1902, [iii], 27, 1138; 1903, [iii], 29, 683), Dilthey and Last (*Ber.*, 1904, 37, 2639), and others have shown that Grignard reagents act normally on succinic esters, producing ditertiary glycols, and in some cases anhydrides of the glycols (Acree, *Amer. Chem. J.*, 1905, 33, 180). The reaction with alkyloxysuccinic esters follows the same course, the products being the corresponding optically active mono- and di-alkoxyglycols or their anhydrides. The action of magnesium phenyl bromide on methyl methoxysuccinate is, however, more complex, and is described in the succeeding paper.

With magnesium methyl iodide, methyl *d*-dimethoxysuccinate ( $[\alpha]_D + 81.04^\circ$  in methyl alcohol solution) gave levorotatory *γ*-*d*-dimethoxy- $\beta$ -*d*-methylheptane- $\beta$ -diol,



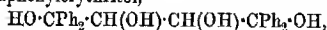
(m. p. 71°,  $[\alpha]_D - 30.9^\circ$  in methyl-alcoholic solution). On treating the substance with excess of dry silver oxide and methyl iodide in the usual manner, the hydroxyl groups were only very partly

In view of our experience with this alkylation process, the result was a matter of surprise, but it appears that tertiary alcohols resist alkylation by this method. G. D. Lander (Trans., 1900, 77, 732) found this to be the case with triphenylcarbinol, and A. McKenzie and H. Wren (Trans., 1910, 97, 476) have shown that of the two hydroxyl groups of *l*-triphenylethylene glycol; the secondary alcoholic group only is thus methylated.

On distilling the levorotatory glycol repeatedly under the ordinary pressure, it was converted to a large extent into a dextrorotatory liquid anhydride by the loss of one molecule of water.  $\beta$ -Dimethylhexane- $\beta$ -diol (L. Henry, *Compt. rend.*, 1906, 143, 496) gives the unsaturated alcohol,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ , by dry distillation. It is unlikely, however, that dehydration should occur in this fashion in the case of the corresponding dimethoxy-glycol, and the dextrorotatory liquid referred to above is more probably the furan derivative,  $\frac{\text{CH(OMe)}\cdot\text{CMe}_2}{\text{CH(OMe)}\cdot\text{CMe}_2} > \text{O}$ , ring formation having changed the sign of rotation.

With magnesium phenyl bromide, ethyl succinate gives tetraphenyltetramethylene glycol (*acdd*-tetraphenylbutane-*ad*-dione) under ordinary conditions, but Acree (*loc. cit.*) found that with a boiling ethereal solution of the Grignard reagent the only product of the reaction was an anhydride, probably tetraphenyltetramethylene oxide (2:2:5:5-tetraphenyltetrahydrofuran). In our experiments on the action of magnesium phenyl bromide on methyl *d*-dimethoxysuccinate, the reaction mixture was not heated, but an excess of the Grignard reagent was used, and the only product isolated was an anhydride (m. p. 184—185°) of the expected glycol. The compound decolorised alkaline permanganate in the cold only after a long time, and did not combine with bromine; we conclude therefore that it is 3:4-dimethoxy-2:2:5:5-tetraphenyltetrahydro-

furan,  $\frac{\text{CH(OMe)}\cdot\text{CPh}_2}{\text{CH(OMe)}\cdot\text{CPh}_2} > \text{O}$ . The compound is thus the dimethylated oxide of tetraphenylerythritol,



which Frankland and Twiss (Trans., 1904, 85, 1666) obtained by the action of magnesium phenyl bromide on methyl tartrate. Frankland's glycol is strongly dextrorotatory ( $[\alpha]_D + 182.8^\circ$  in ethyl-alcoholic solution); our compound is levorotatory ( $[\alpha]_D - 115.7^\circ$  in benzene solution). The great difference between the rotatory powers of the two compounds is probably attributable in the main to the existence of the ring in the structure of the oxide.

*Optical Rotatory Powers.*

All the mono- and dialkoxysuccinic acids and their derivatives, which have been examined, excepting some salts of bivalent metals and the products of the Grignard reactions, retain the sign of the parent *l*-malic and *d*-tartaric acids, that is to say, the monoalkyloxy compounds are levorotatory, the dialkyl-oxy compounds dextro-rotatory. The rotatory powers are much influenced by the nature of the solvent used, water giving as a rule the lowest, and benzene the highest values. The order of increasing effect on the values is in general as follows: water < methyl and ethyl alcohols < acetone < benzene. We tabulate below in the form of molecular rotations some of the observations recorded in the experimental part of this and the preceding paper, and in earlier communications (Trans., 1895, 67, 949, 979; 1901, 79, 962, 965); also, the results of some unpublished observations. To present the results in comparable form, the molecular rotations of the tartrate derivatives have been halved so as to show the optical effect of one only of the two similar asymmetric groups, and in case of solutions, observations have been selected where concentrations were approximately similar, so far as the available data permitted.

*l-Malic derivatives.*

	Solvent.	$[M]_D^{20}$
<i>l</i> -Methoxysuccinic:		
Acid .....	Acetone	-88.9°
Chloride .....	Benzene	100.2
Anhydride .....	Acetone	109.1
Dimethyl ester. Pure liquid		98.9
Diethyl " "	" "	102.9
Dipropyl " "	" "	109.0
<i>l</i> -Ethoxysuccinic:		
Dimethyl ester. "	" "	115.9
Diethyl " "	" "	121.0
Dipropyl " "	" "	126.1

*d-Tartaric derivatives.*

	Solvent.	$[M]_D^{20}/2$
<i>d</i> -Dimethoxysuccinic:		
Acid .....	Acetone	+85.2°
Chloride .....	Benzene	111.9
Anhydride .....	Acetone	119.0
Dimethyl ester. Pure liquid		85.0
Diethyl " "	" "	105.3
Dipropyl " "	" "	111.2
<i>d</i> -Diethoxysuccinic:		
Dimethyl ester. "	" "	106.1
Diethyl " "	" "	124.3
Dipropyl " "	" "	125.3

Dimethyl methoxysuccinate is liquid, dimethyl dimethoxy succinate solid (m. p. 52–53°). The values given for these esters are therefore for 60°. The former ester has  $[M]_D^{20}$  -96.8°; the value calculated for the latter should be about +90° at 20°.

In both series the conversion of acid into anhydride is attended by extensive change of rotatory power, as is commonly the case in ring formation. The acids, it will be seen, are the least optically active of the compounds mentioned, whilst the anhydrides show values of the same order as the more active esters. The conversion of acid into chloride also raises the rotation, but to a less extent. The value for dimethoxysuccinyl chloride, namely 85.8°, is, in fact,

but little higher than that for the acid in the same solvent. With respect to the direction of the change of rotation attending the conversion of acid into chloride, ester, and anhydride, optically active acids of the succinic type show a general regularity which may be stated thus: the changes of rotatory power attending the conversion of alkyloxy-, acyloxy-, and halogen-succinic acids of the same configuration into chloride, ester, or anhydride are similarly directed, the rotation of the *d*- and *l*-acids being always shifted in the dextro- and levo-direction respectively. Keeping in view the fact that *l*-malic and *d*-tartaric acids have an opposite configuration, the rotations of the acids derived from the former are accordingly shifted by the conversions mentioned in the levo-direction, the rotations of those derived from the latter in the dextro-direction. The regularity in question is illustrated in the preceding and following tables. The values quoted below are molecular rotations calculated from specific rotations to be found in Long's translation of Landolt's "Optical Rotating Power." The value given for *l*-bromosuccinic acid is taken from Walden's observation on its enantiomorph, and those for acetylmalic acid and its anhydride from Picot (*Compt. rend.*, 1893, 116, 1134). Where no solvent is indicated, the observations refer to the pure liquid:

	[M] <sub>D</sub>			
	Acid.	Chloride.	Ethyl ester.	Anhydride.
<i>l</i> -Acetylmalic .....	-37° to -45° Acetone.	—————→	-52°2'	→ -41°1' Chloroform.
<i>l</i> -Chlorosuccinic .....	+80°3' Ethyl acetate.	→ +55°5'	→ +57°3'	→ +41°5' Ethyl acetate.
<i>l</i> -Bromosuccinic .....	+133°3' Ether.	—————→	+103°6'	•
<i>d</i> -Diacetyltartaric.....	-55°3' Ethyl alcohol.	—————→	+14°5'	→ +126°8' Benzene.
<i>d</i> -Dibenzoyltartaric .....	-417°0' Ethyl alcohol.	—————→	-245°7'	→ +436°0' Acetone.

The only exception to the general uniformity shown in the table is the low rotation of *l*-acetylmalic anhydride, but this is doubtless explained by the lowering influence of the solvent used (see Walden's observation on methyl acetylmalate in chloroform solution, *Ber.*, 1906, 39, 675). The dextrorotatory halogen-succinic acids are now recognised to have the same configuration as *l*-malic acid, and the direction of the changes of rotation is in agreement with this view.

The direction of the change of rotation in passing from acid to ester in the case of malic and tartaric acids also follows the rule stated. Malic esters are more levorotatory than malic acid. The

molecular rotation of tartaric acid in dilute aqueous solution, it is higher than that of pure ethyl tartrate, but the values found under such different conditions are not comparable. The ester is more dextrorotatory than the acid when both are examined in aqueous solution, or when the acid in organic solvents is compared with the liquid ester. Tartaric acid is, in fact, levorotatory in a mixture of acetone and ether.

We have previously drawn attention (Trans., 1901, 79, 964) to the unexpected general similarity of the molecular rotations of corresponding mono- and di-alkoxy succinic esters. The similarity is remarkable in view of the divergent rotations of malic and tartaric esters, and of their respective mono- and di-acyl derivatives. Fresh data included in the table illustrate still further the regularity referred to. It will be seen that in the case of the esters, and of the acids in acetone solution, the correspondence of the values of the mono- and di-alkoxy-compounds is remarkably close, that is to say, the introduction of OR into  $\text{CH}_2\text{CO}_2\text{R}$  or into  $\text{CH}_2\text{CO}_2\text{H}$  produces remarkably little change on the optical effect of the asymmetric group. The only exceptions are the commonly irregular methyl esters of the series, in which the substitution produces a decided fall of rotation. In general, the introduction of the second alkoxy-radicle is attended by a slight rise of the value. The considerable rise noticeable in the case of the acids, chlorides, and anhydrides is possibly related to the accompanying change of molecular aggregation, the monomethoxy-compounds being liquids, and the dimethoxy-compounds solids at the ordinary temperature.

#### EXPERIMENTAL.

The *l*-methoxysuccinic acid used in the following preparations was obtained from methyl malate by the methods already described (p. 1517).

***l*-Methoxysuccinyl Chloride.**—To 11 grams (1 mol.) of dry *l*-methoxysuccinic acid, 80 c.c. of benzene and 40 grams (2.5 mols.) of phosphorus pentachloride were added, and the mixture was heated for two hours on a water-bath under a reflux condenser. After distilling off benzene and phosphoryl chloride under diminished pressure, the residual liquid gave, on repeated fractionation, 5.7 grams of liquid distillate, b. p. 114—117°/56 mm.:

Found, Cl=37.02.

$\text{C}_6\text{H}_8\text{O}_3\text{Cl}_2$  requires Cl=38.33 per cent.

The rapid decomposition of the chloride when exposed to moist air accounts for the low analytical result. The persistence of the methoxyl group in the acid chloride was confirmed by treating it with methyl alcohol, when methyl *l*-methoxysuccinate was produced.

The specific rotation,  $-51.9^\circ$ , of an acetone solution of the crude, once distilled ester so obtained agreed fairly with that of the initial ester,  $-53.1^\circ$ , prepared from methyl malate. When warmed with water, the chloride dissolved gradually, and, on evaporation, the initial crystalline acid was recovered. The specific rotation of the acid chloride in benzene solution was  $[\alpha]_D^{20} -54.18^\circ$ ,  $c=6.4317$ .\*

The chloride was also prepared by the combined action of acetyl chloride and phosphorus pentachloride on the acid, and the product showed practically the same rotatory power, namely,  $-54.08^\circ$ ,  $c=5.0667$ , but in some experiments this method gave a mixture of chloride and anhydride, which had to be separated by fractional distillation.

#### *l-Methoxysuccinic Anhydride.*

This compound was obtained by heating the dry acid with about four times its weight of acetyl chloride, and distilling the product under diminished pressure. Thirty-one grams of acid gave 22 grams of the crude anhydride, from which, after repeated fractionation, 11 grams of the pure liquid were collected (b. p.  $130-132^\circ/17$  mm.). Analysis gave:

Found, C=45.92; H=4.73; OMe=24.29.

$C_4H_3O_3(OMe)$  requires C=46.13; H=4.66; OMe=23.86 per cent.

In acetone solution,  $[\alpha]_D^{20} -83.91^\circ$ ,  $c=5.6783$ , and in benzene solution,  $-103.3^\circ$ ,  $c=4.9973$ .

#### *Methyl Hydrogen l-Methoxysuccinate.*

On boiling a methyl-alcoholic solution of the anhydride, and distilling the product, the acid ester was obtained as a strongly acid oil (b. p. about  $145^\circ/10$  mm.), which after some time suddenly crystallised. It was very soluble in ordinary organic solvents, less so in petroleum of high boiling point, containing a little ether, from which it separated in tufts of radiating needles, melting at  $46-48^\circ$ .

Found, C=43.89; H=6.44; OMe=38.33.

$C_4H_4O_3(OMe)_2$  requires C=44.42; H=6.23; OMe=38.28 per cent.

Ten c.c. of an aqueous solution of the acid ester required 12.0 c.c. of standard baryta solution for neutralisation, the calculated quantity being 11.8 c.c.

In aqueous solution,  $[\alpha]_D^{20} -41.85^\circ$ ,  $c=6.3086$ , and  $-43.28^\circ$ ,  $c=3.1543$ . In acetone solution,  $-60.86^\circ$ ,  $c=6.9747$ , and  $-57.64^\circ$ ,  $c=3.4874$ . A weighed portion of the acid ester was exactly

\* All the polarimetric observations recorded in this paper were taken in a 2-dm. tube.

neutralised with potassium hydroxide; the specific rotation of the aqueous solution of methyl potassium methoxysuccinate, so obtained, was  $[\alpha]_D^{20} -19.05^\circ$ ,  $c=3.936$ .

#### 1-Methoxysuccinamic Acid.

Succinimide was first obtained by d'Arcet (*Ann. Chim. Phys.*, 1835, [ii], 58, 294) by heating succinic anhydride in a current of dry ammonia gas. This process, when applied to methoxysuccinic anhydride, gave a hard, glassy product, soluble in water, which could not be obtained crystalline. When dry ammonia gas was passed into the anhydride at  $100^\circ$ , a pasty, crystalline mass of mixed plates and needles resulted. The former were isolated by repeated crystallisation from methyl alcohol, and finally from a mixture of ethyl alcohol and ether, and proved to be methoxysuccinamic acid (m. p.  $144^\circ$ ); the needles were apparently the ammonium salt of this acid. In other similarly conducted experiments, the acid alone was produced. The compound was readily soluble in methyl and ethyl alcohol, also in acetone, slightly so in ether, insoluble in benzene, chloroform, carbon tetrachloride, or ethyl acetate:

Found, C=40.64; H=6.35; N=9.64; OMe=19.91.

$C_4H_5O_3N(OMe)$  requires C=40.78; H=6.18; N=9.54;  
OMe=21.09 per cent.

In aqueous solution,  $[\alpha]_D^{20} -29.41^\circ$ ,  $c=4.7777$ , and in methyl-alcoholic solution,  $-46.75^\circ$ ,  $c=3.251$ .

Distillation of the acid gave a crystalline product (m. p.  $59-61^\circ$ ) having an acid reaction; it evolved ammonia on being heated with potassium hydroxide solution, and approximated in composition to methoxysuccinimide. The substance will be further examined.

#### d-Dimethoxysuccinyl Chloride.

The material used in this and the following preparations was procured by methylation of methyl tartrate and conversion of the resulting methyl dimethoxysuccinate into the corresponding acid through decomposition of the barium salt (*Trans.*, 1901, 79, 957). The melting point found for methyl dimethoxysuccinate was two degrees higher than formerly recorded (*loc. cit.*), namely,  $52-53^\circ$ . The rotatory power of the ester in benzene solution was identical with that previously given (solvent: acetone,  $c=5.4183$ ,  $[\alpha]_D^{20} 79.63^\circ$ ). An attempt to prepare the acid chloride from the ester by the direct action of phosphorus pentachloride having proved unsuccessful, the dry acid, partly dissolved in benzene, was treated with this reagent in slight excess of the calculated quantity. The reaction having been completed by heating the mixture for some

time on a water bath, the benzene was distilled off. By washing the solid residue with petroleum of high boiling point, and crystallising it from anhydrous ether, the acid chloride was obtained in long, slender prisms, melting at 90—93°. The yield of crystallised chloride from 27.5 grams of acid was 18 grams:

Found, C=33.19; H=3.94; Cl=32.29.

$C_8H_8O_4Cl_2$  requires C=33.49; H=3.76; Cl=32.98 per cent.

The analytical figures showed that the methoxyl groups had not been attacked by the phosphorus pentachloride. This was confirmed by the reproduction of the initial crystalline methyl dimethoxysuccinate when the chloride was treated with methyl alcohol. With water, the chloride gave crystalline dimethoxysuccinic acid. The specific rotation of the chloride in acetone solution is  $[\alpha]_D^{20}$  79.85°,  $c$  5.3913; in chloroform, 56.87°,  $c$  1.2484; in benzene, 104.14°,  $c$  2.0357.

#### *d-Dimethoxysuccinic Anhydride.*

This compound was readily obtained in well-defined, apparently cubical crystals (m. p. 80—82°) by heating the acid with four times its weight of acetyl chloride, distilling off the excess of the reagent under diminished pressure, and recrystallising the residual product from chloroform and finally from anhydrous ether. Nine grams of acid gave 7 grams of recrystallised anhydride. The previously recorded failure to obtain the compound by this method (Trans., 1901, 79, 960) was doubtless due to the action of water contained in the solvent ether. The dry barium salt, obtained by hydrolysis of the methyl ester, may be substituted with advantage for the acid in the above preparation:

Found, C=44.68; H=5.19; OMc=38.87.

$C_4H_2O_3(OMe)_2$  requires C=44.98; H=5.05; OMc=38.77 per cent.

In acetone solution,  $[\alpha]_D^{20}$  148.7°,  $c$  5.2573, and 148.4°,  $c$  2.3148. By adding a little water to the acetone solution, heating for some time, and evaporating, the crystalline acid was reproduced.

#### *Methyl Hydrogen d-Dimethoxysuccinate.*

On distilling the product obtained by boiling a methyl-alcoholic solution of the anhydride, a viscous, acid syrup was collected (b. p. 137—142°/16 mm.), which analysis showed to be the above compound. Owing to the viscid nature of the product, the separation of the distilled fractions was imperfect, and the substance was probably not pure: \*

In a later preparation, the undistilled product was obtained crystalline, but it was found to be contaminated with dimethoxysuccinic acid.



Found,  $C=43.73$ ;  $H=6.31$ .

$C_8H_{12}O_4$  requires  $C=43.72$ ;  $H=6.31$  per cent.

In acetone solution,  $[\alpha]_D^{25} 91.22^\circ$ ,  $c=4.615$ ; in aqueous solution,  $59.35^\circ$ ,  $c=4.823$ .

*Action of Sodium Methoxide on Methyl 1-Methoxysuccinate.*

A mixture of the ester (1 mol.) and sodium methoxide (2 mols.) in methyl-alcoholic solution was heated at  $60^\circ$  for four hours. On evaporating off the alcohol and pouring the residual oil into ice-cold sulphuric acid, a pale yellow, flocculent solid was precipitated, which was collected and dried on a porous plate in a vacuum desiccator. In a series of experiments under varying conditions, the weight of solid product amounted to only about a tenth of the weight of ester used. For analysis, the substance was precipitated by adding petroleum of high boiling point to its solution in benzene, and dried in a vacuum:

Found,  $C=51.31$ ;  $H=4.71$ ;  $OMe=33.81$ .

$C_8H_8O_4(OMe)_3$  requires  $C=51.54$ ;  $H=4.73$ ;  $OMe=36.35$  per cent.

The low result found for methoxyl is probably accounted for by the incomplete action of the hydriodic acid, due to resinification of the substance. The composition therefore is that of a compound produced by the condensation of 2 molecules of methyl methoxysuccinate with the loss of 3 molecules of methyl alcohol.

*Action of Magnesium Methyl Iodide on Methyl d-Dimethoxysuccinate.*

Twenty grams (1 mol.) of the ester in ethereal solution were added slowly to the ice-cold ethereal solution of the Grignard reagent, prepared from 10.5 grams ( $4\frac{1}{2}$  atoms) of magnesium and 62 grams ( $4\frac{1}{2}$  mols.) of methyl iodide. The product was boiled for one hour, and then decomposed in the usual manner. The crude product was crystallised from light petroleum. Nine grams of *γδ*-dimethoxy-*βε*-dimethylhexane-*βε*-diol, melting at  $71^\circ$ , were obtained:

Found,  $C=58.43$ ;  $H=10.66$ ;  $OMe=31.76$ .

$C_{12}H_{20}O_4(OMe)_2$  requires  $C=58.19$ ;  $H=10.77$ ;  $OMe=30.09$  per cent.

It crystallises in needles, and is very slightly soluble in water, soluble in alcohol, ether, or benzene, less so in light petroleum. In methyl-alcoholic solution,  $[\alpha]_D^{25} -30.9^\circ$ ,  $c=3.5244$ ; and in acetone solution,  $-41.96^\circ$ ,  $c=5.0884$ .

Attempts to acylate and to methylate the compound were not successful. Benzoyl chloride had no action on it, whether applied

by the Schotten-Baumann method, or by heating in ethereal solution in the presence of dry sodium carbonate. The process of methylation by means of dry silver oxide and methyl iodide, carried out in the usual manner, with a large excess of alkylating agent, gave a liquid distillate. Estimations of methoxyl in different fractions of this product gave 39.3, 39.4, and 40.9 per cent., which seemed to show that one of the hydroxyl groups of the glycol had been methylated, the figure calculated on this assumption being 39.3 per cent. In view, however, of the very indefinite boiling point of the liquid, we conclude that methylation had in reality only occurred to a slight extent, and that the increase of methoxyl content, shown by the figures quoted, was mainly due to the unmethylated glycol being dehydrated in the course of the distillation.

Dehydrating agents having failed to give a crystalline anhydride, the glycol was subjected to distillation under the ordinary pressure. When rapidly heated, the compound distilled largely unchanged, but when heated slowly, water was given off, and, after repeated distillations, the crystalline matter disappeared and a colourless oil of camphor-like odour was collected (b. p. 181—186°). The following analysis agrees with the supposition that the oil was a mixture of an anhydride, produced by the loss of 1 molecule of water, with about 19 per cent. of unaltered glycol.

Found, C=62.74; H=10.70.

$C_{10}H_{20}O_3$  requires C=63.76; H=10.73.

The composition of the mixture was not affected by further distillation. An acetone solution gave  $[\alpha]_D^{20}$  13.35°,  $c=4.495$ . The anhydride therefore, in contradistinction to the parent glycol, is dextrorotatory. On heating the acetone solution with an equal bulk of water in a sealed tube at 105°, the rotatory power underwent no change, and the anhydride therefore, as was to be expected, is not readily reconverted into the glycol.

*Action of Magnesium Phenyl Bromide on Methyl d-Dimethoxy-succinate: Preparation of 3:4-Dimethoxy-2:2:5:5-tetra-phenyltetrahydrofuran.*

When the ester (1 mol.) dissolved in ether was added to an ethereal solution of the Grignard reagent (4 mols.), and the mixture, after being heated for some time, was treated as usual with dilute sulphuric acid, no crystalline substance was isolated from the product. In the following experiment, other conditions being the same, the proportion of the Grignard reagent was increased to 6 molecules, and the mixture was kept overnight without heating. On mixing the ethereal solutions, a considerable action took place,

and two layers were formed. The product having been treated in the usual manner, the separated ethereal layer gave, on evaporation, a syrup, which crystallised immediately. The crystalline matter, freed from adhering oil by draining on a porous plate and washing with cold methyl alcohol, amounted to 16 grams. The substance crystallised from ethyl alcohol in beautiful iridescent leaflets, but the indefinite melting point of the recrystallised material, 162—180°, showed that it was impure. By further recrystallisation from petroleum of high boiling point, the melting point was raised to 184—186°:

Found, C=82.79; H=6.65.

$C_{30}H_{23}O_3$  requires C=82.51; H=6.33 per cent.

Finally, by dissolving in benzene and adding ether, a crop of crystals (8 grams) was deposited in flat prisms. When these were heated at 120—130°, they became powdery, probably from escape of adhering solvent, and then melted sharply at 184—185°.\* (Found, C=82.06; H=6.63.) On distilling in a current of steam, no diphenyl could be detected.

The substance was saturated, as it was not attacked after remaining twelve hours in a carbon disulphide solution of bromine.

In attempting to estimate methoxyl in the usual way, no action was perceptible, and after the process the substance was recovered unchanged. Even in the presence of acetic anhydride resinification occurred, and the action of the hydriodic acid was very incomplete. By heating the substance with a mixture of acetic anhydride and hydriodic acid in a sealed tube at 200°, and completing the analysis in the usual apparatus according to Zeisel's method, a result approximating to the calculated figure was obtained:

Found, OMe=12.87.

$C_{25}H_{23}O(OMe)_2$  requires OMe=14.22 per cent.

The compound is insoluble in water and in aqueous alkali, moderately soluble in hot alcohol, more so in acetone and in warm light petroleum, and very soluble in chloroform or benzene. In benzene solution,  $[\alpha]_D^{20} = -115.7^\circ$ ,  $c=8.272$ .

We wish to thank Miss M. A. Dunbar for assistance given in part of the experimental work.

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\* From further experiments, we have reason to believe that the true melting point is considerably higher than is recorded, and that the crude product (m. p. 162—180°) contained a compound of lower melting point, which was not isolated.

**XLII.—Action of Grignard Reagents on Methyl *l*-Methoxysuccinate, Methyl Maleate, and Maleic Anhydride.**

By THOMAS PURDIE, F.R.S., and PAUL SEIDELIN ARUP, B.Sc.

It has been shown in the preceding paper that magnesium methyl iodide and magnesium phenyl bromide act on methyl *d*-dimethoxysuccinate in the same manner as on unsubstituted succinic esters. Magnesium methyl iodide gives  $\gamma\delta$ -dimethoxy- $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol, and the phenyl bromide yields 3:4-dimethoxy-2:2:5:5-tetraphenyltetrahydrofuran. The etheric methoxyl groups are not attacked in either case, and the products are therefore optically active.

We find that the action of magnesium methyl iodide on methyl *l*-methoxysuccinate is similar to that of the same reagent on the dimethoxy-ester, the product being optically active  $\gamma$ -methoxy- $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol,  $\text{HO}\cdot\text{CMe}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{OH}$ . The glycol, however, could not be obtained in the pure state. The product, being a liquid, was isolated by distillation in a vacuum, and this caused partial dehydration. By distillation under atmospheric pressure, complete dehydration was effected, and the final product obtained was the oxide of the glycol (a furan derivative), or possibly an isomeric unsaturated alcohol. In acetone solution, the compound gave  $[\alpha]_D + 44.9^\circ$ . Calculating the rotatory power of the glycol in acetone solution from that of a mixture with the anhydride, the approximate composition of which was determined by the results of analysis, the value should be about  $[\alpha]_D + 35^\circ$ . The initial ester being levorotatory, the conversion of ester into glycol results in a change of sign of rotation. This is also the case in the production of the corresponding dimethoxyglycol from the dimethoxy-ester (see the preceding paper). But whilst the conversion of the latter glycol into its oxide brings about a second reversal of the sign, in the dehydration of the monomethoxyglycol the sign remains the same. This difference is not in agreement with the usual optical effect of ring formation, and suggests that the dehydration referred to above proceeds on different lines, giving possibly an unsaturated alcohol.

The action of magnesium phenyl bromide on methyl *l*-methoxysuccinate proved to be more complex than that of magnesium methyl iodide. Two crystalline compounds were isolated from the product of the reaction, having respectively the composition  $\text{C}_{22}\text{H}_{22}\text{O}$  (m. p.  $190\text{--}191^\circ$ ) and  $\text{C}_{22}\text{H}_{18}\text{O}_2$  (m. p.  $160\text{--}161^\circ$ ), but

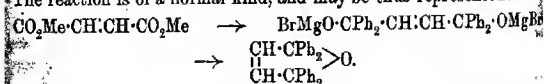
either contained methoxyl, and both were optically inactive. The former substance was found to be 2,2,5,5-tetraphenyl-2,5-dihydrofuran,

$\begin{array}{c} \text{CH} \cdot \text{CPh}_2 \\ | \\ \text{CH} \cdot \text{CPh}_2 \end{array} > \text{O}$ , and the latter a triphenylbutyrolactone.

The unsaturated character of the dihydrofuran derivative was exhibited in its behaviour towards bromine, with which it readily combined, and by its rapidly decolorising cold alkaline permanganate solution. The constitution was deduced from the following observations. Oxidation by boiling dilute alkaline permanganate solutions gave benzophenone. Distillation with zinc dust, according to Baeyer's process, gave a hydrocarbon,  $\text{C}_{28}\text{H}_{20}$  (m. p. 157—158°), and reduction of this with sodium and amyl alcohol gave the *acdd*-tetraphenylbutane,  $\text{CHPh}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHPh}_2$ , which Valeur (*Bull. Soc. chim.*, 1903, [iii], 29, 683) obtained similarly from tetraphenylbutadiene,  $\text{CPh}_2 \cdot \text{CH} \cdot \text{CH} \cdot \text{CPh}_2$ . The hydrocarbon  $\text{C}_{28}\text{H}_{20}$  agrees in melting point and composition with a hydrocarbon obtained by Buitenberg (*Annalen*, 1894, 279, 329) from the action of concentrated sulphuric acid on  $\beta\beta$ -diphenylvinyl ether,  $\text{CPh}_2 \cdot \text{CH} \cdot \text{OEt}$ , and the substances are presumably identical. The only formula for the hydrocarbon, consistent with the results of its reduction, as given above, with the molecular weight found by us, and with Buitenberg's method of preparation, appears to be  $\text{CPh}_2 \cdot \text{C} \cdot \text{C} \cdot \text{CPh}_2$ .

The constitution of the dihydrofuran derivative suggested that the disappearance of the methoxyl group was due to the abstraction of a molecule of methyl alcohol from the monomethoxysuccinate with the production of a maleic or fumaric ester or other derivative, which was then further acted on by the Grignard reagent. We accordingly examined the action of magnesium phenyl bromide on methyl fumarate and maleate and on maleic anhydride.

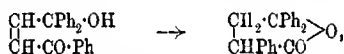
Methyl fumarate gave an uncrystallisable syrup, the examination of which yielded no definite result. Methyl maleate, however, gave the same tetraphenyldihydrofuran which has been already described. The reaction is of a normal kind, and may be thus represented:



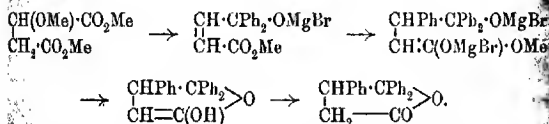
It appears, therefore, that in the case of methyl methoxysuccinate, methyl alcohol is split off from the ester at the outset, or at an early stage, of the Grignard reaction, which otherwise follows the normal course. The second product of the action of magnesium phenyl bromide on methyl methoxysuccinate has been already referred to as triphenylbutyrolactone (m. p. 160—161°); we assign a lactonic structure to the compound on the following grounds.

The substance showed neither alcoholic nor ketonic properties, and behaved as a saturated compound. It dissolved sparingly, and only on prolonged boiling, in aqueous potassium hydroxide and ammonia solutions. It was, however, converted by boiling alcoholic potash into a potassium salt, which, after removal of the alcohol, dissolved completely in water. The aqueous solution of the salt gave with mineral acids a white, flocculent precipitate, which was soluble with effervescence in cold sodium carbonate solution, and was doubtless hydroxytriphenylbutyric acid. The precipitated acid, after being dried at 90°, melted at 140–145°, and still decomposed warm sodium carbonate solution, but after being heated for an hour at 130°, it was no longer soluble in sodium carbonate, and then showed the melting point of the original substance, 160°.

With respect to the position of the three phenyl groups, we regard the compound provisionally as  $\beta\gamma\gamma$ -triphenylbutyrolactone, for the following reasons. As the substance gives benzophenone on oxidation, two of the phenyl groups must be attached to the same carbon atom, and without assumption of improbable transposition, this can only be the  $\gamma$ -carbon atom. The phenyl groups must therefore be in the  $\alpha\gamma\gamma$ - or  $\beta\gamma\gamma$ -positions. The former constitution implies a transposition of the following kind:



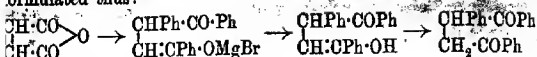
which is certainly not improbable. A  $\beta\gamma\gamma$ -lactone, however, might result normally from the Grignard reaction according to the following scheme:



The addition of the Grignard reagent is here supposed to take effect in the 1:4-position, which Kohler has found to be a common mode of action with unsaturated ketones and esters (*Amer. Chem. J.*, 1904, 31, 642, etc.).\* We failed to obtain evidence of this mode of addition in the case of methyl maleate, but we find, on the other hand, that maleic anhydride reacts with magnesium phenyl bromide, probably in the manner in question, the product being A. Smith's

\* If direct addition of the Grignard reagent to the two unsaturated carbon atoms occurs, then either an  $\alpha\gamma\gamma$ - or  $\beta\gamma\gamma$ -lactone might be formed. The action is, in other respects, like that described by Shibata in the case of the phthalic esters (*Trans.*, 1909, 95, 1449).

benzoylacetophenone (Trans., 1890, 57, 643). The action may be formulated thus:



The triphenylbutyrolactone (m. p. 160–161°) sublimes unchanged when heated alone under diminished pressure, but when heated with mineral acids it is converted nearly quantitatively into an isomeric lactone, melting at 197°. The latter substance resembled the former in giving benzophenone on oxidation, in its behaviour as a saturated compound, and in its insolubility in cold alkali hydroxide solutions. It dissolved, however, much more readily than the former lactone in boiling aqueous potassium hydroxide and ammonia solutions, and the acid which was precipitated on acidification—presumably a triphenylhydroxybutyric acid—lost its solubility in sodium carbonate, and regained the original melting point, 197°, on being simply dried in a vacuum without heating. The solution of the potassium salt coagulated to a jelly on cooling, which redissolved on sufficient water being added. A silver salt of the corresponding hydroxy-acid was precipitated on adding silver nitrate to an ammonia solution of the lactone after the excess of ammonia had been boiled off. After being dried at 100°, it gave  $\text{Ag}=24.87$ ;  $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Ag}$  requires  $\text{Ag}=24.59$  per cent. The production of the lactone just described might be accounted for by the migration of a phenyl group, but we refrain from discussing the nature of the isomeric change until the two lactones and the acids derivable from them have been further examined.

#### EXPERIMENTAL.

The methyl *l*-methoxysuccinate used in the following experiments was obtained by methylating methyl malate by means of dry silver oxide and methyl iodide.

The boiling point of the liquid ester was 135°/42 mm., and it gave  $[\alpha]_D^{20} - 54.2^\circ$ .

#### Action of Magnesium Methyl Iodide on Methyl *l*-Methoxysuccinate.

Preliminary experiments showed that the product of the action was an uncrystallisable oil. Using four molecular proportions of the Grignard reagent to one of the ester, the carbon content of the distilled product indicated that the action was incomplete, but with excess of the reagent, a liquid of lower boiling point was obtained having approximately the composition of an anhydride of the ditertiary glycol, which was expected to result from the

reaction. In the following experiment, therefore, an excess of the Grignard reagent was employed.

Ten grams of the ester (1 mol.), dissolved in ether, were added slowly to an ethereal solution of magnesium methyl iodide, prepared from 10 grams (7.4 atoms) of magnesium. After the brisk reaction which ensued had subsided, the mixture was heated for three hours on a water-bath, and thereafter decomposed in the usual way with dilute sulphuric acid. The product was then thoroughly extracted with ether. The dried ethereal solution gave, on evaporation, a brownish oil, which was distilled under diminished pressure. Some water was produced during the distillation, presumably from decomposition of the glycol, and 10 grams of a colourless, mobile liquid, with a camphoraceous odour, were collected at 60–90°/90 mm. After distilling this twice, a fraction (b. p. 63–64°/33 mm.), weighing 4.5 grams, was obtained, which gave, in acetone solution,  $[\alpha]_D^{20} + 42.5^\circ$  ( $c=2.2336$ ), and on analysis  $C=66.75$ ,  $H=11.36$ ,  $OMe=19.3$ . The expected ditertiary glycol,  $C_8H_{17}O_2(OMe)$ , requires  $C=61.36$ ,  $H=11.36$ ,  $OMe=17.61$  per cent.; its anhydride,  $C_{16}H_{34}O(OMe)$ , requires  $C=68.35$ ,  $H=11.39$ ,  $OMe=19.62$  per cent.

The liquid was presumably a mixture of the ditertiary glycol and its oxide, the latter having been produced by the elimination of water in the course of the distillation. As it was found that but little increase of the carbon content was brought about by further distillation under diminished pressure, the liquid was now distilled under the atmospheric pressure. A fraction collected after two distillations (b. p. 150–151°) gave  $C=67.88$ ,  $H=11.39$ ,  $OMe=19.17$ .

The substance is therefore a dehydration product of the glycol,  $\gamma$ -methoxy- $\beta$ -dimethylhexane- $\beta$ -diol. A cryoscopic determination of the molecular weight in benzene solution gave 152;  $C_8H_{15}O(OMe)$  requires 158. The specific rotation in acetone solution was  $[\alpha]_D^{20} 44.9^\circ$ ;  $c=3.9185$ ,  $l=2$ .

#### *Action of Magnesium Phenyl Bromide on Methyl l-Methoxysuccinate.*

The conditions observed in the following experiment were found to be the most advantageous in respect of the yield of crystalline product. Thirty grams of the ester (1 mol.) in ethereal solution were added slowly to an ethereal solution of the Grignard reagent prepared from 33 grams of magnesium (8 atoms) and 215 grams of bromobenzene (8 mols.) A vigorous reaction occurred. After remaining twelve hours at the ordinary temperature, the mixture was treated with ice-cold dilute sulphuric acid in the usual manner. On evaporating the ethereal layer, successive crops of crystals were deposited, in all 44 grams, which were found to consist of two



substances melting at  $190^{\circ}$ – $191^{\circ}$  and  $160^{\circ}$ – $161^{\circ}$ , respectively. The separation of these was effected by dissolving each of the crops in benzene and adding one and a-half times as much ether to each solution. This treatment precipitated the much less soluble compound of higher melting point, and, on concentrating the mother liquors, the compound melting at the lower temperature was deposited. By systematic repetition of the process, 7.5 grams of each substance were obtained nearly pure; the remaining material consisted mostly of the compound (m. p.  $160^{\circ}$ – $161^{\circ}$ ), which was the main crystalline product of the reaction.

As already stated, the compound melting at  $190^{\circ}$ – $191^{\circ}$  is 2:2:5:5-tetraphenyl-2:5-dihydrofuran, and the compound melting at  $160^{\circ}$ – $161^{\circ}$  a triphenylbutyrolactone.

2:2:5:5-Tetraphenyl-2:5-dihydrofuran crystallises from a mixture of benzene and ether in fine needles. It is moderately soluble in cold benzene, sparingly so in cold alcohol, acetone, or petroleum of high boiling point, but fairly soluble in the hot solvents, and almost insoluble in boiling ether. It crystallises unchanged from hot glacial acetic acid:

Found, C=89.56; H=6.00.

$C_{26}H_{20}O$  requires C=89.84; H=5.88 per cent.

The following observations are in accord with the constitution assigned to the compound. A 6 per cent. solution in benzene at  $40^{\circ}$  was optically inactive. On applying Zeisel's process for estimating methoxyl to a solution of the substance in acetic anhydride, no silver iodide was formed, even when the temperature was raised to  $130^{\circ}$ . An alcoholic solution of the compound reduced alkaline permanganate instantly in the cold. On adding bromine (2 atoms) in carbon disulphide solution to the compound (1 mol.) in the same solvent, an additive compound was evidently formed, as the colour of the bromine disappeared quickly in the dark, and a crop of yellow, acicular crystals was deposited. On attempting to recrystallise the substance, however, decomposition occurred with liberation of hydrogen bromide, and estimation of bromine in different preparations gave varying figures approximating to those required for a monobromo-derivative.

Oxidation of the furan derivative with a boiling dilute alkaline solution of potassium permanganate gave benzophenone. The product was isolated by distillation in a current of steam, and was identified by its melting point ( $48^{\circ}$ ), and by that of the phenyl-hydrazone prepared from it ( $136^{\circ}$ ).

The reduction of the compound was effected by distilling 9.5 grams with zinc dust in a current of hydrogen at a temperature considerably below a red heat. The distillate solidified, on cooling, to

an amber-colored glass, which was deposited in a crystalline state from a solution in a mixture of ethyl alcohol and ether. After three crystallisations from this medium, 2.4 grams of colourless, rectangular plates were obtained, melting at 157–158°. The substance was sparingly soluble in alcohol, readily so in ether, benzene, or chloroform, and decolorised cold alkaline permanganate instantly.

Found, (I),  $C=93.85$ ;  $H=5.80$ . (II)  $C=94.17$ ;  $H=5.94$ .

$C_{22}H_{20}$  requires  $C=94.38$ ;  $H=5.62$  per cent.

The molecular weight in chloroform solution, determined by the ebullioscopic method, was 364.  $C_{22}H_{20}$  requires 356.

One gram of the hydrocarbon was dissolved in 50 c.c. of boiling amyl alcohol, and 10 grams of sodium were added in small pieces. The hot solution was then poured into a mixture of 400 c.c. of water and 7 grams of glacial acetic acid. The alcoholic layer, evaporated under diminished pressure to half its bulk, gave 0.4 gram of crystalline, rectangular plates, which, after being recrystallised from ethyl alcohol, melted at 121°. The substance resembled stilbene, but it was found that admixture with pure stilbene caused a considerable lowering of the melting point, and, moreover, it decolorised cold dilute alkaline permanganate only after some time. (Found,  $C=92.47$ ;  $H=6.93$ . Calc.,  $C=92.82$ ;  $H=7.18$  per cent.) This hydrocarbon, as already stated, is *ααδδ*-tetraphenylbutane.

*Triphenylbutyrolactone* (m. p. 160–161°), which was isolated, as already described, from the crude product of the action of the Grignard reagent, crystallises in microscopic needles. It is readily soluble in cold acetone or chloroform, moderately so in cold ether, sparingly so in cold alcohol and benzene, but fairly soluble in the latter solvents when hot. At 200°/20 mm. it sublimes unchanged in beautiful prisms:

Found, (I)  $C=83.85$ ;  $H=6.01$ . (II)  $C=83.91$ ;  $H=5.98$ .

$C_{22}H_{18}O_2$  requires  $C=84.08$ ;  $H=5.73$  per cent.

The molecular weight in chloroform solution, determined by the ebullioscopic method, was 337.  $C_{22}H_{18}O_2$  requires 314.

The compound was optically inactive. Only a trace of silver iodide was formed when 2 grams of it were heated with hydriodic acid for one and a-half hours according to Zeisel's process. It was not affected by heating with an alcoholic solution of hydroxylamine for nine hours at 160°, by boiling for three hours with acetyl chloride, or by shaking with benzoyl chloride and sodium hydroxide solution. In each case, the substance was recovered unchanged after the treatment. It decolorised an alkaline solution of potassium permanganate in the cold only slowly, and it was recovered unaltered after being twelve hours in contact with bromine in carbon disulphide solution. Oxidation with boiling dilute alkaline per-

manganate solution gave benzophenone, which was identified by conversion into the oxime. The lactonic behaviour of the compound has been already described.

*Action of Mineral Acids on Triphenylbutyrolactone*  
(m. p. 160—161°).

In testing for methoxyl by Zeisel's method in an impure fraction obtained by crystallising the crude product of the Grignard reagent, 2 grams of the material, melting about 140°, were boiled with hydriodic acid (D 1.7) for one and a-half hours. The residual solid from this treatment, after being washed with water and a little alcohol, and recrystallised from benzene, weighed 1.6 grams, and now melted at 192—196°. Similar treatment of the pure triphenyl-lactone (m. p. 160—161°) showed that the change of melting point was due to the apparently quantitative conversion of this compound into an isomeric lactone, melting at 197°. The same change occurred when the lactone of lower melting point was heated with concentrated hydrochloric acid in a sealed tube, or with sulphuric acid (70 per cent. by volume) for two hours at 140°.

*Triphenylbutyrolactone* (m. p. 197°) crystallises from chloroform or benzene in well-defined, prismatic needles. It is insoluble in water, moderately soluble in cold ether and acetone and in hot benzene, readily so in hot chloroform, but sparingly soluble in the two latter solvents or alcohol when cold. The compound proved to be optically inactive:

Found, (I) C=84.22; H=5.89. (II) C=84.10; H=5.81.

$C_{22}H_{18}O_2$  requires C=84.08; H=5.73 per cent.

By oxidation with boiling dilute alkaline permanganate solution, 1 gram of the substance gave 0.4 gram, nearly the calculated yield, of benzophenone (m. p. 47—49°). Baeyer's permanganate test showed that the compound was saturated, and this was confirmed by its resistance to a cold solution of bromine in carbon disulphide. After being in the bromine solution for twelve hours, the compound was recovered unchanged. The lactonic properties of the substance have been already described in the introduction.

*Action of Magnesium Phenyl Bromide on Methyl Maleate.*

Methyl maleate was prepared by the interaction of methyl iodide and silver maleate, the latter being obtained from maleic anhydride. Twenty grams of the anhydride gave 23 grams of the ester (h. p. 201—205°).

Ten grams of methyl maleate (1 mol.) were treated with magnesium phenyl bromide obtained from 6.7 grams of magnesium

(4 atoms) and 44 grams of bromobenzene (4 mols.). The procedure was the same as in the previous cases. After the spontaneous vigorous action had subsided, the mixture was heated for an hour on the water-bath, and then treated in the usual manner. The ethereal layer, on evaporation, left a syrup which deposited crystalline matter after some time. The syrup having been removed by stirring the product with a little ether, 2 grams of residual solid were collected and recrystallised by dissolving it in benzene and adding ether. By repeating the process, 1.2 grams of pure substance were obtained in fine, colourless needles, which melted sharply at  $190^{\circ}$ . The solubilities of the compound, the melting point, and the results of analysis showed it to be the same 2:2:5:5-tetraphenyl-2:5-dihydrofuran already described as one of the products of the action of the Grignard reagent on methyl methoxysuccinate. (Found, C=89.41; H=6.14. Calc., C=89.84; H=5.88 per cent.)

The syrup which constituted the main product of the reaction was distilled under diminished pressure, but diphenyl was the only crystalline substance found in it. The syrup was hoiled with hydriodic acid in the hope that the lactone (m. p.  $197^{\circ}$ ) might be produced, but without result.

*Action of Magnesium Phenyl Bromide on Maleic Anhydride.*

The method pursued was the same as in the action with methyl maleate. The materials were 10 grams of maleic anhydride (1 mol.) and magnesium phenyl bromide prepared from 11 grams of magnesium (4.5 atoms) and 72 grams of bromobenzene (4.5 molecules). The reaction was vigorous, and was moderated by cooling in ice. The mixture was heated for an hour after spontaneous action had ceased, and was then treated in the usual manner. The oil, left on evaporating the ethereal extract, soon deposited crystalline matter, which was collected and washed with a little alcohol. The total isolated product consisted of 10 grams of nearly pure crystalline substance, and about an equal weight of uncrystallisable oil. The crystals, after being once recrystallised from alcohol containing a few drops of acetic acid and once from absolute alcohol, melted sharply at  $126-127^{\circ}$ . (Found, C=84.16; H=5.93.  $C_{22}H_{16}O_2$  requires C=84.08; H=5.73 per cent.)

The substance was therefore isomeric with the two lactones previously described; but its insolubility in potassium hydroxide solution on long hoiling showed that its character was neither acidic nor lactonic. It proved to be identical with A. Smith's desylacetophenone (Trans., 1890, 57, 643) ( $\alpha\beta$ -diketo- $\alpha\beta\beta$ -triphenylbutane), which he found to be converted into 2:4:5-triphenylfuran (m. p.  $92^{\circ}$ ) by cold concentrated sulphuric acid. On following Smith's

... ABSORPTION SPECTRA OF ANILINE ...  
 ... from our previous work ...  
 ... a crop of acicular crystals which melted at 92° and ...  
 ... the furan derivative referred to. The identity was con-  
 ... by analysis. (Found, C=88.85; H=5.62. Calc., C=89.19;  
 H=5.41 per cent.)

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### CXLIII.—*The Absorption Spectra of Aniline and its Homologues as Vapours, as Liquids, and in Solution.*

By JOHN EDWARD PURVIS.

THE aim of this communication is to give an account of a comparative study of the absorption spectra of aniline and its liquid homologues, in the state of vapours, liquids, and in solution, in order to ascertain, under these conditions, (1) the nature of the influence on the absorption of the radiant energy, and (2) how far the replacement of the hydrogen atoms by simple groups in the nucleus, or in the side-chain, affects the extent and type of the absorption bands.

The substances examined were aniline, mono- and di-methyl-aniline, mono- and di-ethylaniline, *o*- and *m*-toluidine, *o*-3-xylydine, *m*-2-xylydine, mesidine, and benzylamine. The substances were distilled several times before use.

#### EXPERIMENTAL.

##### *Vapours.*

The absorption spectrum of the vapour of aniline in a tube 1-dm. long, and at 35°, has been studied by Pauer (*Wied. Ann.*, 1897, 61, 374), who measured the positions of sixteen absorption bands, employing the radiant energy of the Cd spark. More recently, Grebe (*Dis.*, Bonn, 1905; and *Zeitsch. wiss. Photochem.*, 1905, 3, 363) studied the vapour of aniline at 25–30°, and used the continuous spectrum obtained when a powerful spark was passed between aluminium poles immersed in water. He noted the presence, and measured the positions of twenty-eight bands. Neither of these observers, however, investigated the effect of varying the temperature and pressure.

The author has already given an account of the absorption spectra of the vapours of pyridine and some of its derivatives (this

vol. III, 1922, pp. 1-10, and the apparatus used in this investigation is described in the first cited paper. Each band was separately measured at the different temperatures and pressures, and on the more refrangible edge.

*Aniline.*

TABLE I.

The absorption bands in aniline vapour at various temperatures and pressures in a column 2-cm. long. Barometric pressure = 763 mm.

Abbreviations: w.=weak; mod. str.=moderately strong; str.=strong; v.w.=very weak; r.w.=rather wide; narr.=narrow; mod. w.=moderately weak; v. str.=very strong. The brackets of the wave-lengths represent the measurements of similar related bands; they are not measurements of the width of the bands.

14°. 763 mm.	30°. 807 mm.	45°. 833 mm.
λ.	λ.	λ.
2978 w.	2978 mod.w.	2981 w., narr.
2977 w.	2977 w.	2978 mod.str., narr.
2975·5 w.	2974·5 mod.str.	2977 w.
2973 w.	2973 mod.w.	2975 str., narr.
2969·5 w.	2970·5 mod.str.	2973 mod.str.
2966·5 mod.str.	2967 "	2970·5 mod.str., wider than 2973
2964 w.	2964 w., r.w.	2966·5 mod.str.
2961·5 mod.str.	2962 mod.str.	2963 "
2958 " "	2959 "	2962 "
2953·5 w.	2954·5 w., r.w.	2958·5 " narr.
2951 w.	2951·5 w., r.w.	2954·5 w., wide
2949 w.	2950·5 mod.str., narr.	2951 "
2945 mod.str.	2946 "	2949 mod.str., narr.
2942·5 str.	2943 v.str.	2946 "
2940 wider and stronger than 2942·5	2940 wider and stronger than 2943	2942·5 str., wide "
2935 mod.str.	2934 mod.str.	2939 " "
2931 v.w. } equally	2930 w.	2934 str., narr.
2928 v.w. } strong	2927·5 w.	2931 w., wide
2923·5 v.w.	2924 w.	2928·5 "
2921·5 v.w.	2921·5 w., narr.	2924·5 "
2919 mod.str.	2918 str.	2921·5 w., narr.
2914 str.	2913·5 wider and stronger than 2918	2918 str., wide
2912·5 v.w.	2912·5 v.w.	2915·5 " "
2909 v.w.	2910 w., wide	2912 v.w.
2907 v.w.	2907 w., narrower than 2910	2909·5 w., narr.
2901 mod.str.	2900 mod.str., narr.	2906 w., wide
2897·5 str.	2897 str.	2900 "
2894 v.w.	2894 v.w.	2897 v.w., wide
2891·5 w.	2891 mod.str., narr.	2893 w.
2879 v.w.	2878·5 w., narr.	2891 mod.str., wide
2877 v.w.	2877·5 "	2878·5 v.w.
2875 v.w.	2876 "	2877·5 v.w.
2874 v.w.	2875 "	2876 v.w.
2871 v.w.	2872 "	2875 v.w.
2870 v.w.	2871 "	2872 v.w.
2868 w., wide	2866 w., wide	2871 v.w.
2866 w., wide	2866 "	General absorption began about λ 2850.
2864 w., narr.	2866 "	86 bands.
2862 w., narr.	2866 "	

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763 mm.	807 mm.	865 mm.
$\lambda$ .	$\lambda$ .	$\lambda$ .
2859.5 str., wide	2864 w., narr.	3005 v.w., wide
2867 mod.str.	2862 w., stronger than 2864	3000 " "
2868 w., narr.	2859.5 str., wide	2995 w., narr.
2863.5 v.w.	2857 mod.str.	2993 v.w., narr.
2861.5 v.w., narr.	2856 w., narr.	2989 " "
2848.5 " "	2854.5 " "	2985 mod.str., wide
2846 " "	2851.5 v.w., narr.	2978 " "
2844 " "	2849 " "	2975 " "
2841 " "	2847 " "	stronger than 2878
2838 " "	2844.5 v.w., f.wide	2972 mod.str., wide
2838 " "	2841.5 " "	2970 " "
2834.5 w.	2838 w., narr.	2968 " "
2832 w.	2836 " "	2962 " "
2830 mod.w.	2834.5 " "	2958.5 " "
2828 " "	2832.5 " "	
2826.5 " "	2830.5 r.w.	General absorption began at about $\lambda$ 2940; the Cd line 2948 was just visible.
2821 head of wide band	2828 " "	
2814.5 v.w.	2826.5 " "	
2810.5 v.w.	2821 head of strong wide band	13 bands.
2807 v.w., stronger than other two	2818 w., narr.	
2804.5 mod. str.	2812 " "	
2798.5 w.	2808.5 " "	
2794.5 w.	2805 mod.str.	
2791.5 w.	2799 w., r.w.	
2787 w., wide	2795 " "	
2782 w., wide	2791.5 " "	75°.
2781 v.w.	2787 " "	893 nm.
2779 v.w.	2783 " "	
2770 v.w.	2781 v.w.	$\lambda$ .
2768.5 v.w.	2778 v.w., narr.	3005 w., wide
2766 v.w.	2770.5 w., narr.	3000 " "
2764.5 v.w.	2768.5 " "	2995 " "
2760 v.w.	2766.5 " "	2993 " "
2757.5 v.w.	2765.5 " "	2989 " "
2755 v.w.	2759.5 mod.str., wide	2985 " "
2739 v.w.	2757.5 w., narr.	General absorption began at about $\lambda$ 2980.
2737 v.w.	2754 mod.str., narr.	
2729 w.	2744 v.w., narr.	
2730 mod.str.	2743 " "	6 bands.
2726 v.w.	2740 w., wide	
2725 v.w.	2737.5 " "	
2722 v.w.	2729 mod.str.	
2720.5 v.w., wide	2730 stronger than 2729	
2717.5 " "	2726.5 w., narr.	
	2725 " "	
General absorption began at about $\lambda$ 2400; Cd lines 2821, 2813, 2288, 2266, 2194, 2144 were just visible.	2723 " "	90°.
	2720.5 w., wide	923 nm.
	2717.5 " "	$\lambda$ .
	General absorption began at about $\lambda$ 2430.	No bands and general absorption began at about $\lambda$ 3070.
83 bands.	85 bands.	

The absorption spectrum of aniline vapour was also observed at a constant temperature of 17.5° and at gradually diminished pressures. The number and position of the bands were the same

as those observed at 14° and 763 mm. pressure in the above table, but they became sharper and weaker as the pressure decreased, and the position of general absorption was shifted towards the more refrangible regions of the spectrum. For example, under 754 mm. pressure the general absorption began at about  $\lambda$  2400, the Cd lines 2329, 2321, 2313, 2288, 2265, 2194, 2144 were very weak; under 474 mm. pressure the general absorption began at about  $\lambda$  2390, and the Cd lines beyond were stronger; whilst under 24 mm. pressure the general absorption began at about  $\lambda$  2370, and the Cd lines were very strong.

The bands are more of the nature of strong lines than of what is usually understood by a band; and the width of many of them is measurable to the same degree and in the same sense as the images of many of the bright lines in emission spectra. They are not nearly so wide as an Ångström unit, and the width of some of the narrow bands is not measurable at all. The constitution and appearance of the bands is completely different from those of the vapour of benzene as described by Hartley (*Phil. Trans.*, 1907, A, 208, 475). Most of the latter appear to be wide bands, sharp and strong on the more refrangible edge.

The results prove that (1) an increase in the temperature and pressure produces a strengthening and widening of the bands, and the appearance of new bands on the less refrangible side; (2) a decrease in the pressure, the temperature remaining constant, produces a weakening and narrowing of the bands. At the same time, (3) an increase in the temperature and pressure produces a shift of the region of general absorption towards the red end; whilst (4) a decrease in the pressure, the temperature remaining constant, produces a shift in the opposite direction.

The bands observed in the vapour of aniline occur chiefly as a series of doublets and triplets; some of them are sharper on the more refrangible edge, whilst others have the edges equally sharp; some of the doublets appear to be equally strong, and some of them show the less refrangible of the two not quite so strong as the more refrangible one. Of the triplets, some have the three constituents equally strong, and of others the most refrangible constituent is the strongest. In addition to these general observations, an attempt has been made to arrange the bands in a definite and regular manner. The following table indicates fairly consistent differences in the wave-lengths of the majority of the bands, considered as a whole:



# PREVIS: THE ABSORPTION SPECTRA OF AMTANT AND ITS

3000					2985				
35	3000				31	2978			
2970	33	2995			2954	27	2977		
30	2967	31	2993		33	2951	25	2975	
2940	32	2964	31	2989	2921	32	2949	30	2973
38	2985	33	2962	80	42	2919	35	2945	30
2907	34	2931	84	2959	2879	42	2914	33	2943
	2901	34	2928	35	19	2977	39	2912	34
2870	33	2897	34	2924	2860	20	2875	38	2909
21	2868	31	2894	33	24	2857	19	2874	38
2849	21	2866	30	2891	2836	23	2856	20	2871
	2847	22	2864	29	31	2834	24	2854	20
2827	26	2844	23	2862	2805	35	2832	24	2851
45	2821	29	2841	24	39	2799	37	2830	23
2782	40	2815	29	2838	2766	34	2795	38	2828
43	2781		2812	29	41	2765	36	2792	
2739	44		42	2809	2725	43	2759	34	
	2737		2770	40		2722	39	2758	
			40	2769			2720	41	
			2730	43				2717	
				2726					

The numbers run consecutively from left to right and diagonally, and the differences are differences in Ångström units between successive band intervals.

In addition to the regularity observed from comparing the whole of the bands, there are various minor groups which appear to be related. Of these, the following are a series of well-marked doublets whose most refrangible constituent is the strongest:

2978.0	3.5	2949	4	2918.0	4.5	2901	4
2974.5		2945		2913.5		2897	

or, if the corresponding members of each group are arranged in tabular form, the following differences are observed:

2978	29	2974.5	29.5
2949	31	2945.0	31.5
2918	17	2913.5	16.5
2901		2897.0	

The following are a series of narrow doublets of similar appearance, the constituents of which are equally strong:

2879	2	2875	1	2871	1	2838	2	2834.5	2
2877		2874		2870		2836		2832.5	

The bands 2830, 2828, 2826 are equally strong, and form a group by themselves with a constant difference of about 2 units; and the bands 2815, 2811, 2807 form a group whose most refrangible constituent is the strongest, and there is a constant difference between them of about 4 units.

Photographs of the absorption spectra, in the 2-dcm. tube, of the vapour of the following substances were also taken under varying degrees of temperature and pressure.

### Monomethylaniline.

14°	755	The rays were transmitted to about $\lambda$ 2500 and then absorbed; of the Cd lines, 2321, 2313, 2288, 2265, 2194, 2144 were just visible.
30	799	The rays were transmitted to about $\lambda$ 2750 and then absorbed; the Cd line 2573 was just visible.
45	825	The rays were transmitted to about $\lambda$ 3050, and then all the rays beyond were absorbed.
60	855	The rays were transmitted to about $\lambda$ 2990 and then absorbed.
75	885	The rays were absorbed from about $\lambda$ 3130.
90	915	" " " $\lambda$ 3150.
100	931	" " " $\lambda$ 3165.

### Dimethylaniline.

12.5	765	The rays were absorbed from about $\lambda$ 2500, but the strong Cd lines 2321 to 2144 were just visible.
30	805	The rays were absorbed from about $\lambda$ 2750, but the Cd line 2573 was visible.
45	835	The rays were absorbed from about $\lambda$ 3020, although the Cd line 2981 was visible.
60	865	The rays were absorbed from about $\lambda$ 3070.
75	895	" " " $\lambda$ 3120.
90	925	" " " $\lambda$ 3140.
100	941	" " " $\lambda$ 3170.

### Monoethylaniline.

13.5	765	The rays were absorbed from about $\lambda$ 2470, but the strong Cd lines 2321 to 2144 were just visible.
30	805	The rays were absorbed from about $\lambda$ 2540.
45	835	" " " $\lambda$ 2700, but the Cd line 2573 was well marked.
60	865	The rays were absorbed from about $\lambda$ 3050.
75	895	" " " $\lambda$ 3080.
90	925	" " " $\lambda$ 3120.
100	941	" " " $\lambda$ 3150.

### Diethylaniline.

12	766	The rays were transmitted to about $\lambda$ 2450, and the Cd lines 2329 to 2144 were well marked.
100	942	The rays were absorbed from about $\lambda$ 3150.

### o-Toluidine.

13	760	The rays were transmitted to about $\lambda$ 2470; the Cd lines from 2329 to 2144 were well marked.
30	804	The rays were transmitted to about $\lambda$ 2540; the Cd lines 2321, 2313, 2288, 2265, 2194, 2144 were visible.
45	830	The rays were transmitted to about $\lambda$ 2700; the Cd line 2573 was just visible.
60	860	The rays were transmitted to about $\lambda$ 2980; the Cd line 2748 was just visible.
75	890	The rays were transmitted to about $\lambda$ 3060.
90	920	" " " $\lambda$ 3100.
100	936	" " " $\lambda$ 3120.

*m-Toluidine.*

	Pressure in mm.	
13	759	The rays were transmitted to about $\lambda$ 2480; the Cd lines 2329 to 2144 were well marked.
45	829	The rays were transmitted to about $\lambda$ 2750, the Cd line 2748 ending sharply; the Cd line 2573 was just visible.
75	839	The rays were transmitted to about $\lambda$ 3050; the Cd line 2980 was just visible.
100	935	The rays were transmitted to about $\lambda$ 3110.

*o-3-Xylidine* (b. p. 223°).

12	752	The rays were transmitted to about $\lambda$ 2400; the Cd lines 2329 to 2144 were well marked.
30	796	The rays were transmitted to about $\lambda$ 2450; the Cd lines 2329 to 2144 were visible.
60	852	The rays were transmitted to about $\lambda$ 2800; the Cd line 2573 was well marked.

*m-2-Xylidine* (b. p. 215°).

12	752	The rays were transmitted to about $\lambda$ 2250; the Cd lines 2194 and 2144 were well marked.
30	796	The rays were transmitted to about $\lambda$ 2380; the series of Cd lines from 2329 to 2144 were well marked.
60	852	The rays were transmitted to about $\lambda$ 2470; the Cd lines from 2329 to 2144 were visible.

*Mesidine* (b. p. 233°).

13	759	The rays were transmitted to about $\lambda$ 2350; the Cd lines 2321 to 2144 were strong.
45	829	The rays were transmitted to about $\lambda$ 2420; the Cd lines 2321 to 2144 were well marked.
75	839	The rays were transmitted to about $\lambda$ 2550; the Cd lines 2313 and 2268 were just visible.
100	935	The rays were transmitted to about $\lambda$ 3000; the Cd lines 2830, 2837, and 2748 were visible.

*Benzylamine.*

12.5	752	The rays were transmitted to about $\lambda$ 2250; the Cd lines 2194 and 2144 were well marked.
30	796	The rays were transmitted to about $\lambda$ 2250; the Cd lines 2194 and 2144 were visible.
45	822	The rays were transmitted to about $\lambda$ 2420; the Cd lines from 2329 to 2144 were well marked.
60	852	The rays were transmitted to about $\lambda$ 2500; the Cd lines from 2329 to 2144 were visible.
75	882	The rays were transmitted to about $\lambda$ 2650; the Cd line 2573 was well marked.
90	910	The rays were transmitted to about $\lambda$ 2900; the Cd lines 2830, 2837, and 2748 were visible.

*General Results of the Absorption Spectra of the Vapours.*

The results of the preceding observations of the absorption spectra of the vapours of aniline and its homologues prove that (1) aniline vapour has a considerable number of absorption bands which show relationships amongst themselves both in structure and in differences of wave-lengths; (2) under the influences of increased temperature and pressure the aniline bands become wider; weak bands become stronger; new bands make their appearance; and the general absorption is shifted towards the less refrangible region; (3) with decreased pressure, the temperature remaining constant, the aniline bands become sharper and weaker, and the region of general absorption is shifted towards the more refrangible region of the spectrum; (4) the most remarkable fact is that none of the homologues of aniline show any of the bands characteristic of aniline; (5) under the influences of increased temperature and pressure, the general absorption of the vapours of the homologues of aniline is shifted towards the less refrangible region.

*Solutions.*

The experimental methods employed in the study of the absorption spectra of solutions have been described before.

*Aniline, Monomethylaniline, and Dimethylaniline.*—The ultra-violet absorption spectra of alcoholic solutions of aniline have been described by Hartley and Huntington (*Phil. Trans.*, 1879, 170, I, 257), who observed two bands at  $\lambda$  285— $\lambda$  274 and  $\lambda$  240— $\lambda$  230. Baly and Collie (*Trans.*, 1905, 87, 1342) state that they repeated the observations with identically the same results. They also plotted the absorption curves of the bands in alcoholic solutions of monomethylaniline and dimethylaniline, and they show that the difference in the persistence of the band in the three cases is very marked. The absorption curve of dimethylaniline showed also a second band on the more refrangible side. The author found similar results to those of Baly and Collie in  $N/1000$ -solutions of these three substances, and the curves are therefore not reproduced.

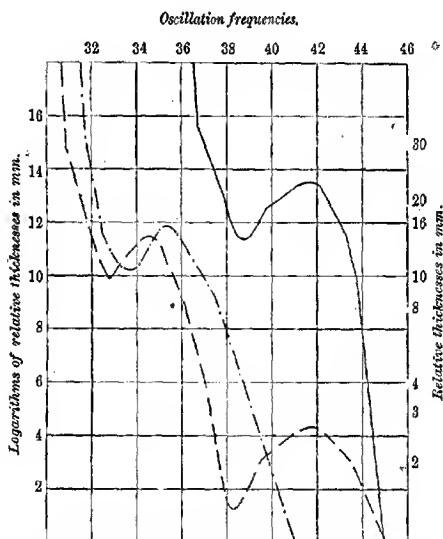
*Monoethylaniline and Diethylaniline.*—The author has investigated the absorption spectra of the ultra-violet regions of  $N/1000$ -alcoholic solutions of these substances. It will be noticed (Fig. 1) that diethylaniline shows a second band at about  $1/\lambda$  3850, which is absent in monoethylaniline. It is precisely similar to the phenomena observed by Baly and Collie in mono- and dimethylaniline. It is also noticeable that the characteristic band of these substances is not so persistent as the corresponding bands in aniline, mono- and dimethylaniline.

large, persistent band, the head of which was about  $1/\lambda$  3040.  
*m-Toluidine*.—Baly and Ewbank (Trans., 1905, 87, 1358) described a large, persistent band, the head of which was about  $1/\lambda$  3045.

The author has repeated the observations with  $N/1000$ -solutions of *o*-toluidine and *m*-toluidine, and found similar results. The curves therefore are not reproduced.

*o*-3-Xylidine and *m*-2-Xylidine.— $N/1000$ -alcoholic solutions of

FIG. 1.



Continuous curve:  $N/100$ -alcoholic solution of benzylamine.  
 Dot and dash curve:  $N/1000$ -alcoholic solution of monoethylamine.  
 Dash curve:  $N/1000$ -alcoholic solution of diethylamine.

these substances were observed, and their absorption curves have been drawn (Fig. 2). The general form of the curves is not unlike that of the toluidines. The bands are strongly persistent, and their positions are more towards the red end than the corresponding bands of the toluidines.

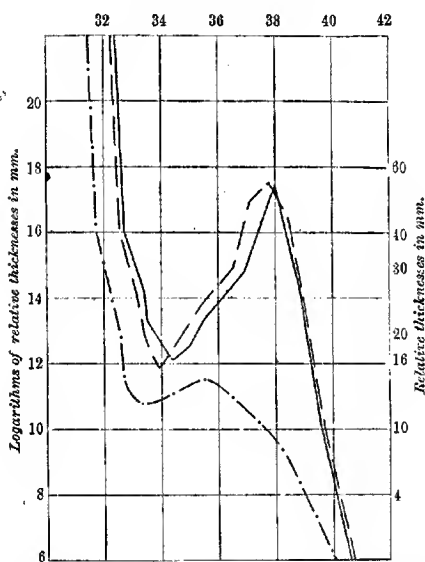
*Mendine*.—An  $N/1000$ -solution of this substance exhibits a band which is not very persistent (Fig. 2). It is of some interest to note

that the persistency of this band is not so marked as that of either the toluidines or the xyldines.

*Benzylamine.*—An  $N/1000$ -solution transmitted the rays to about  $\lambda 2290$  through a thickness of 30 mm., but an  $N/100$ -solution showed a moderately strong band, the curve of which has been drawn (Fig. 1). The position of this band is more towards the regions

FIG. 2.

Oscillation frequencies.



Continuous curve:  $N/1000$ -alcoholic solution of  $o$ -3-xyldine.  
 Dash curve:  $N/1000$ -alcoholic solution of  $m$ -2-xyldine.  
 Dot and dash curve:  $N/1000$ -alcoholic solution of mesidine.

of greater refrangibility than in any of the substances herein described. It is of some importance to notice that the band corresponds in position and general form with the band  $1/\lambda 3850$  of diethylaniline.

#### General Results of the Absorption Spectra of the Solutions.

The general results of the investigation of the absorption spectra of the solutions are that (1) in the replacement of the hydrogen

of the amino-group of aniline by alkyl groups, the persistence of the curve, is considerably reduced; (2) when the hydrogen of the nucleus is replaced by alkyl groups the band becomes large and persistent; (3) in mesidine the band is not very strong or persistent, and (4) in benzylamine the band is fairly strong.

### Liquids.

Hartley and Huntington (*Phil. Trans.*, 1879, **170**, I, 274) pointed out that it was only on dilution that the absorption bands of aromatic substances became visible. The thickness of the layer of liquid used by them was 0.75 inch.

In investigating the absorbent effect of liquids a special form of cell was used. It consisted of two quartz plates firmly cemented to a brass box or telescope. One of the quartz plates was attached to a movable micrometer screw, which could be moved by thousandths of a mm., whilst the other plate was rigidly attached to a brass stage. A drop of the liquid to be investigated was placed between the two quartz plates, and these were then screwed together to a distance of 0.05 mm. apart. The screw was turned so that the quartz plate attached to it was moved closer and closer to the rigidly placed plate until the distance between them was about 0.001 mm. The light of the Cd spark was passed through the film of liquid for five minutes during each observation. Even through the thinnest films of about 0.001 mm. no absorption bands were seen; and the following numbers state the regions where general absorption began under the above conditions, and through various thicknesses of the films.

<i>Aniline.</i>		<i>Methylaniline.</i>		<i>Dimethylaniline.</i>		<i>Ethylaniline.</i>	
Thickness of film, mm.	$\lambda$ .	Thickness of film, mm.	$\lambda$ .	Thickness of film, mm.	$\lambda$ .	Thickness of film, mm.	$\lambda$ .
0.050	3185	0.050	3305	0.050	3310	0.050	3260
0.030	3175	0.030	3295	0.030	3300	0.030	3250
0.010	3160	0.010	3270	0.010	3280	0.010	3220
0.004	3150	0.004	3260	0.004	3260	0.004	3210
0.001	3140	0.001	3250	0.001	3270	0.001	3200
<i>Diethylaniline.</i>		<i>o-Toluidine.</i>		<i>m-Toluidine.</i>		<i>o-S-Xylidine.</i>	
0.050	3325	0.050	3150	0.050	3180	0.050	3175
0.030	3310	0.030	3135	0.030	3170	0.030	3165
0.010	3285	0.010	3120	0.010	3140	0.010	3150
0.004	3275	0.004	3100	0.004	3130	0.004	3140
0.001	3265	0.001	3095	0.001	3125	0.001	3130

<i>m</i> -2- <i>xyloidine</i>		<i>Mesidine</i>		<i>Benzylamine</i>	
Thickness of film, mm.	$\lambda$ .	Thickness of film, mm.	$\lambda$ .	Thickness of film, mm.	$\lambda$ .
0.050	3200	0.050	3250	0.050	2745
0.030	3180	0.030	3210	0.030	2735
0.010	3160	0.010	3160	0.010	2730
0.004	3145	0.004	3140	0.004	2720
0.001	3140	0.001	3130	0.001	2710

### *General Results of the Absorption Spectra of the Liquids.*

The more important points of interest in the above table are that (1) the constitution of the molecules of the various compounds influences the general absorption. For example, the positions of general absorption of the ortho compounds are different from those of the isomeric meta-compounds; the differences in this respect are comparable with the differences observed in the absorption of their solutions; (2) isomeric substances like benzylamine, the toluidines, and methylaniline show differences in their positions of general absorption, which are also analogous to differences in the absorption of their solutions; (3) none of the substances when in the liquid condition exhibit absorption bands through the thinnest films of 0.001 mm. thick.

It is not possible to imply very much from these numbers, as it is conceivable that films thinner than 0.001 mm. are obtainable under greater pressure, which would allow more of the ultra-violet vibrations to pass through. On the other hand, such excessively thin films produced by pressure could no longer be considered as liquids. The physical condition of the molecules would then be more of the nature of a vapour under high pressure, and the results would hardly be comparable.

### *Discussion of Results.*

In discussing the preceding observations we are confronted with the fact that the vapours of toluene, the xylenes, and mesitylene all exhibit absorption bands as described by Pauer, Grebe (*loc. cit.*), and by Hartley (*Phil. Trans.*, 1908, A, 208, 475), and that the number of bands decreases as the number of methyl groups increases; but in the toluidines, not only do the bands of toluene vapour disappear, but also those characteristic of aniline vapour, and similar phenomena are observed in the xyloidines and in mesidine. Further, the replacement of a hydrogen atom of the amino-group in aniline by an alkyl group produces a complete elimination of the bands characteristic of aniline vapour.

In the alcoholic solutions the type of absorption band is very similar in aniline and in the methyl- and ethyl-anilines, whereas



the toluenes and the xylenes the bands are stronger, broader in position, and much more persistent than in either toluene, the xylene, or aniline. The position and intensity of the band in benzylamine is also quite different from that of either toluene or aniline, but it corresponds in form and position with the more refrangible band of diethylaniline.

In the liquids, the general absorption is so great that the ultra-violet light is absorbed over the regions covered by the bands found in the solutions even at thicknesses of the liquids represented by 0.001 mm.

The author has already discussed (*loc. cit.*) the absorption spectra of the vapours of pyridine and some of its derivatives from a consideration of the impacts of symmetrically and unsymmetrically oriented molecules. It seems to be possible to apply a similar explanation to the phenomena described in this communication. In the methyl- and ethyl-anilines the symmetrical orientation of the aniline molecule is distorted, and the vibrations of the more symmetrical aniline, which produce selective absorption, are destroyed. The vibrations producing the absorption bands in the vapours of toluene or the xylenes are wholly different from those producing the bands in aniline vapour; and in the vapours of the toluidines and the xylenes there is no trace of any of the series of bands. The symmetrical orientation of the atoms is absent in these compounds, and the vibrations no longer exercise a selective absorption of the radiant energy. The energy may be chiefly absorbed by the translatory energy of the molecules producing general absorption, which becomes more pronounced as the temperature and pressure are increased.

In the solutions, the solvent acts partly as a constraint on the vibrations of the molecules of the dissolved substance, partly as a barrier to the number of encounters, and partly as an absorbent of a portion of the radiant energy. The result of these influences is that the vibrations of the molecules are quite different from those of the vapours. The atoms of the molecules under these conditions vibrate or oscillate in a definite way characteristic of each substance; and molecules of the same type, for example, aniline and the methyl- and ethyl-anilines, exhibit bands having similar forms. They differ only in their relative positions and in their increased or decreased persistencies, which are regulated by the number, weight, and type of the substituted groups.

In the liquids, the molecules are more closely packed, and they exert a greater tensional effect on each other, so that the restraining influences on the vibrations are still more powerful. The radiant energy is absorbed by the molecules, for even when the film of

In the various liquids, no bands of selective absorption were observed in any of the liquids. Nevertheless, the differences observed in the positions of general absorption of the ortho- and meta-compounds and in the isomeric substances, benzylamine, methylaniline, and the toluidines, indicate that, besides the weight of the molecule, the orientation is also a factor in determining the extent of the general absorption as distinct from selective absorption.

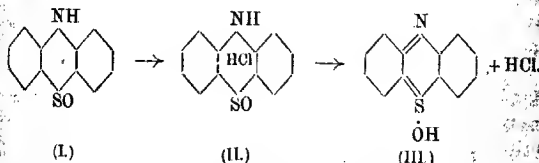
I have again to convey my thanks to the Government Grant Committee of the Royal Society, by whose assistance the larger portion of the cost of the apparatus used in these experiments was defrayed.

UNIVERSITY CHEMICAL LABORATORY,  
 CAMBRIDGE.

#### CXLIV.—*The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides. Part III. The Tri- and Tetra-chlorosulphoxides.*

By OSCAR Lisle BRADY and SAMUEL SMILES.

In the previous communication on this subject (Barnett and Smiles, this vol., p. 186) the mechanism of this reaction was discussed, and it was shown that the rearrangement, which is brought about by the action of acids on the sulphoxides of diphenylamine, probably depends on the preliminary formation of salts of these substances (II):



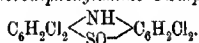
In order to obtain complete confirmation of this hypothesis, it is evidently desirable to isolate these sulphoxide salts and to examine their independent behaviour; but in none of the six cases which have been studied has this been possible. In those instances where the sulphoxide was sufficiently basic to give promise that the salts would be readily formed, the conversion into the phenazobonium

derivative was too rapid to permit of their being isolated, and in other cases, where this conversion is slow, the sulfoxides were of acidic character or such extremely weak bases that no hope of isolating the salts in the pure condition could be entertained.

It has been shown that the conversion of the sulfoxide into the phenazothionium derivative depends on the nature of the groups present in the aromatic nuclei (Barnett and Smiles, this vol., p. 192) of the former, and it appeared not improbable that, in accordance with the usual phenomena of steric hindrance, the mere presence of substituents, whatever their nature, would exert a retarding influence on this change. With this assumption, it is clear that in order to isolate the required salts a sulfoxide must be chosen containing substituents which do not to any great extent depress the basic character of the parent substance, and are present in sufficient number to prevent the conversion into the phenazothionium derivative taking place too readily. Since the chloro-derivatives of thiodiphenylamine appeared to satisfy these requirements, the following experiments were undertaken with them.

Tetrachlorothiophenylamine is easily prepared in large quantities by the simultaneous action of hydrochloric acid and hydrogen dioxide on thiophenylamine (Page and Smiles, this vol., p. 1112). This substance was converted into the sulfoxide in the usual manner by the further action of hydrogen dioxide.

*Tetrachlorodiphenylamine o-Sulphoxide,*



Tetrachlorothiophenylamine was suspended in glacial acetic acid, to which an excess of 30 per cent. hydrogen dioxide had been added. The mixture was set aside at the atmospheric temperature for three or four days. The completion of the reaction was indicated by the disappearance of the characteristic crystals of the sulphide, which were replaced by a very finely divided precipitate. This was collected, and, after the adherent acetic acid had been removed, the solid was recrystallised from benzene. In this way tetrachlorodiphenylamine-*o*-sulphoxide was obtained in colourless prisms, which melted at 220°, the fused mass assuming a reddish-brown colour:

0.1304 gave 0.1931 CO<sub>2</sub> and 0.0186 H<sub>2</sub>O. C=40.4; H=1.6.

C<sub>12</sub>H<sub>6</sub>ONCl<sub>4</sub>S requires C=40.8; H=1.4 per cent.

The presence of the sulfoxide grouping in this compound is proved by the condensation with phenetole to the *S*-phenetyl derivative which is described later.

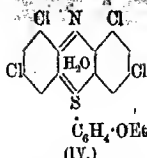
This sulphoxide has been previously prepared, although evidently in an impure condition, by Unger and Hofmann (*Ber.*, 1896, 29, 1362) from the action of nitric acid on tetrachlorodiphenylamine. These authors find that, as usual, the bivalent sulphur is oxidised to the sulphoxide group by that reagent, but that, unless special precautions are taken, a portion of the halogen is displaced by nitro-groups. We have repeated these experiments, and, whilst confirming the observations of Unger and Hofmann, find that the method is not suitable for preparing the pure sulphoxide in large quantity. The product is usually red, and is evidently contaminated with the phenazothionium derivative, which, as will be shown later, is obtained from the sulphoxide by the action of strong acids.

The conversion of this tetrachlorosulphoxide into the phenazothionium hydrate appears to be effected with approximately the same ease as that of the dinitro-sulphoxide (Barnett and Smiles, *Trans.*, 1909, 95, 1261). It is not attacked by dilute mineral acids, and only slowly by hot concentrated hydrochloric acid. In sulphuric acid the reaction is slow, and it can be followed by the change in colour and by the reactions of the solutions. Freshly prepared solutions of the sulphoxide in the concentrated acid, which are of a deep yellowish-brown colour, evidently still contain the sulphoxide, for, on adding phenetole or a similar substance to them, the *S*-arylphenazothionium derivative is formed. However, after the lapse of about four hours, these solutions become violet, and the *S*-phenetyl derivative cannot then be obtained by the addition of phenetole; on pouring the solution into water, the tetrachlorophenazothionium hydrate is precipitated.

*Tetrachloro-S-phenetylphenazothionium.\**

An excess of phenetole was gradually added to a cold solution of tetrachlorodiphenylamine sulphoxide in concentrated sulphuric acid. The course of the reaction is indicated by the appearance of an intense blue colour, and, as soon as it was found that a sample of the solution gave a precipitate of a pure reddish-brown colour on being mixed with water, the addition of phenetole was suspended. On pouring the solution into water, the required derivative was precipitated; it was collected, washed with water, and then converted into the base by trituration with dilute aqueous sodium hydroxide. The substance was again collected, and, after being washed with water until free from alkali, it was dried in the steam-oven, and finally extracted with chloroform in Soxhlet's apparatus. The cold extract deposited tetrachloro-*S*-phenetylphenazothionium hydrate (IV) in chocolate-coloured prisms, which melted at 197°.

BRADY AND SMILES: THE INTERMEDIATE  
 The substance, when prepared in this manner, contains  
 microform of crystallisation, for a sample which had been dried for



some hours in the steam-oven readily furnished phenylcarbylamines  
 when warmed with aniline and alkali hydroxide. Analysis con-  
 firmed this suspicion:

0.1326 gave 0.2047  $\text{CO}_2$  and 0.0242  $\text{H}_2\text{O}$ .  $\text{C} = 42.2$ ;  $\text{H} = 2.6$ .

0.1197 „ 0.1851  $\text{CO}_2$  „ 0.0217  $\text{H}_2\text{O}$ .  $\text{C} = 42.2$ ;  $\text{H} = 2.0$ .

$\text{C}_{20}\text{H}_{13}\text{ONS}\text{Cl}_4 \cdot \text{H}_2\text{O}$  requires  $\text{C} = 50.5$ ;  $\text{H} = 3.1$  per cent.

$\text{C}_{20}\text{H}_{13}\text{ONS}\text{Cl}_4 \cdot \text{H}_2\text{O} \cdot \text{CHCl}_3$  requires  $\text{C} = 42.4$ ;  $\text{H} = 2.8$  per cent.

This additional chloroform is very firmly retained by the sub-  
 stance, for on heating a sample for several hours at  $140-150^\circ$ , only  
 slight loss of weight occurred, and analysis showed that almost the  
 theoretical amount of halogen was still present:

0.1074 gave 0.1697  $\text{AgCl}$ .  $\text{Cl} = 39.1$ .

$\text{C}_{20}\text{H}_{13}\text{ONS}\text{Cl}_4 \cdot \text{H}_2\text{O} \cdot \text{CHCl}_3$  requires  $\text{Cl} = 41.8$  per cent.

The substance is insoluble in water, sparingly soluble in ether, and  
 readily so in other warm organic media. It imparts an intense  
 blue colour to sulphuric acid.

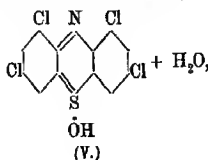
#### *Tetrachlorophenazothionium.*

A solution of tetrachlorodiphenylamine *o*-sulphoxide in concen-  
 trated sulphuric acid was kept at the atmospheric temperature for  
 four or five hours, when it was poured on ice, and the mixture set  
 aside overnight to obtain complete separation of the insoluble  
 material. The latter was then collected, and, after being purified  
 and dried at  $100^\circ$ , it was analysed:

0.1066 gave 0.1532  $\text{CO}_2$  and 0.0181  $\text{H}_2\text{O}$ .  $\text{C} = 39.1$ ;  $\text{H} = 1.9$ .

$\text{C}_{12}\text{H}_5\text{ONS}\text{Cl}_4 \cdot \text{H}_2\text{O}$  requires  $\text{C} = 38.8$ ;  $\text{H} = 1.8$  per cent.

*Tetrachlorophenazothionium hydroxide* (V),



which is obtained in this way as a brownish-red powder, resembles other hydroxides of this series in containing an additional molecule of water (this vol., p. 186). The latter is not readily eliminated; in fact, it is only on heating to about  $180^{\circ}$  that water is expelled, the compound melting somewhat indefinitely at  $200^{\circ}$ . The substance is insoluble in water, but soluble in hot glacial acetic acid. The solutions in sulphuric acid are purple, and do not react with phenetole or similar compounds. This azothionium derivative may also be prepared by direct oxidation of the tetrachloro-sulphide in acid media.

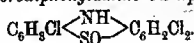
*Oxidation of Tetrachlorothiodiphenylamine.*—(a) *With Chromic Acid.*—A hot solution of tetrachlorothiodiphenylamine was gradually mixed with the calculated amount of chromic acid dissolved in the same medium. The mixture was set aside to cool, and then poured into cold water, the insoluble product being collected and recrystallised from benzene. This was analysed (1).

(b) *With Caro's Reagent.*—The calculated amount of potassium persulphate was slowly added to a cold mixture of tetrachlorothiodiphenylamine and concentrated sulphuric acid. The liquid was poured over crushed ice, and then set aside until the product was completely precipitated. The latter was collected, washed with water until free from sulphuric acid, then dried, and finally recrystallised from hot ethyl acetate. The substance was analysed (2). The product obtained by these two methods forms dark red prisms, which melt at  $220^{\circ}$ , and give purple solutions with concentrated sulphuric acid:

- (1) 0.2142 gave 0.3316  $\text{CO}_2$  and 0.0294  $\text{H}_2\text{O}$ .  $\text{C}=42.2$ ;  $\text{H}=1.5$ .  
 0.1046 „ 0.1700  $\text{AgCl}$ .  $\text{Cl}=39.4$ .  
 (2) 0.1406 „ 0.2184  $\text{CO}_2$  and 0.0216  $\text{H}_2\text{O}$ .  $\text{C}=42.3$ ;  $\text{H}=1.7$ .

It is evident from the analytical data that the substance is not the phenazothionium hydroxide ( $\text{C}=38.8$  and  $\text{H}=1.8$  per cent.) which is obtained by rearrangement of the sulphoxide. According to the numbers which are quoted above, the compound would appear to be either an oxide derived from the phenazothionium hydroxide by separation of the elements of water ( $\text{C}=41.8$  and  $\text{Cl}=41.2$  per cent.) or a compound of the nature of a quinhydrone composed of equal molecular proportions of sulphide and azothionium hydroxide ( $\text{C}=41.7$  and  $\text{Cl}=41.1$  per cent.). The latter alternative appears to be the more probable, but since this question lies outside the scope of the present experiments it has not been further pursued.

The tetrachloro-sulphoxide, the derivatives of which have now been described, is not a sufficiently strong base to furnish stable salts with acids, and attention was therefore turned to the trichloro-derivative.

*Trichlorodiphenylamine o-Sulphoxide,*

In the chlorination of thiodiphenylamine by the action of hydrogen dioxide and hydrochloric acid in alcoholic solution (Page and Smiles, this vol., p. 1118), it was sometimes observed that the yield of tetrachloro-sulphide was considerably below that required by theory. Since this substance is almost insoluble in the alcoholic mother liquor obtained in this preparation, it appeared probable that the loss might be due to incomplete chlorination, hence the more soluble substances produced in this reaction were examined. These were isolated by pouring the filtered mother liquor into a large bulk of water; the solid was collected, washed, dried, and finally recrystallised from hot benzene. The trichloro-sulphoxide was isolated from the less soluble portion obtained in this process. It is readily soluble in hot benzene, and was obtained in prismatic crystals, which melted at 160°. It is soluble in concentrated sulphuric acid, immediately producing an intense violet colour, and when the solution is mixed with water the reddish-brown azothionium derivative is obtained:

0.1125 gave 0.1870 CO<sub>2</sub> and 0.0218 H<sub>2</sub>O. C=45.3; H=2.1.

C<sub>12</sub>H<sub>6</sub>ONCl<sub>3</sub>S requires C=45.2; H=1.9 per cent.

The *hydrochloride* of this sulphoxide was also isolated from the mother liquors of the preparation of tetrachlorothiodiphenylamine by cautiously adding water to them and setting the mixture aside until the precipitate had formed. The substance was purified and dried for analysis in a vacuum desiccator:

0.1216 gave 0.1785 CO<sub>2</sub> and 0.0133 H<sub>2</sub>O. C=40.2; H=1.2.

0.1167 „ 0.1897 AgCl. Cl=40.2.

C<sub>12</sub>H<sub>6</sub>ONCl<sub>3</sub>S.HCl requires C=40.5; H=1.9; Cl=40.0 per cent.

It forms a pale grey powder, which is soluble in concentrated sulphuric acid, giving purple solutions, and evolving hydrogen chloride; the latter is also eliminated when the compound is boiled with water.

The corresponding *trichlorophenazothionium* derivative is formed when this hydrochloride is heated either alone to about 100° with water, or in boiling media, such as benzene or ethyl acetate. Prolonged heating decomposes the product, which is therefore difficult to isolate in a pure state. A weighed quantity of the hydrochloride was suspended in cold water, and the mixture was heated to the boiling point. The reddish-brown product was immediately collected and washed with cold water, the filtrates being collected. Analysis of the product, which melted indefinitely at 125–130°,

and gave the usual reaction of phenazothionium derivatives with sulphuric acid, showed that it was the partly hydrolysed phenazothionium chloride, and this was confirmed by estimation of the free hydrochloric acid in the mother liquors:

0.1186 gave 0.1740  $\text{CO}_2$  and 0.0197  $\text{H}_2\text{O}$ .  $\text{C}=41.8$ ;  $\text{H}=2.0$ .

$\text{C}_{12}\text{H}_{10}\text{NCl}_4\text{S}_2\text{H}_2\text{O}$  requires  $\text{C}=42.8$ ;  $\text{H}=2.3$  per cent.

Further attempts to purify this compound by more prolonged boiling with water or by treatment with alkali hydroxide were not successful on account of its instability towards these reagents.

The fact that this hydrochloride is so readily converted into the azothionium derivative adds further support to the hypothesis already advanced on other grounds that in the change of these sulphoxides of diphenylamine to the azothionium compounds by the action of acids the salts of the former are first produced.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of these experiments.

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#### CXLV.—*The Action of Bases on $\alpha\beta$ -Dibromobutyric Acid and its Esters.*

By THOMAS CAMPBELL JAMES.

In a previous communication (James and Sudborough, *Trans.*, 1909, 95, 1543) it was established that when hydrogen bromide is abstracted from  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid (cinnamic acid dibromide) by the action of feeble bases and alkaloids, the yield of  $\alpha$ -bromocinnamic acid is comparatively much greater, and the amount of  $\alpha$ -bromo-*allo*cinnamic acid correspondingly diminished, than when strong alkalis are used. Thus, when the decomposition is effected by alcoholic potassium hydroxide in the cold, the ratio  $\alpha$ -bromocinnamic acid/ $\alpha$ -bromo-*allo*cinnamic acid is, roughly, 1/7, whereas with trimethylamine it is about 1/2. An increase in the relative amount of the  $\alpha$ -bromo-acid also occurs in experiments with weak bases where heat is required to complete the reaction, but in these cases a considerable amount of decomposition takes place with formation of  $\alpha$ -bromostyrene and evolution of carbon dioxide, and the precise degree of transformation of *allo*-acid into its stereo-



side is thereby obscured. It has been shown by following the reaction between aqueous alkali and  $\alpha\beta$ -dibromobutyric acid, kinetically, that the tendency towards decomposition is less in this case than in the above, and a series of experiments has therefore been carried out to investigate the action of various bases on this acid.

$\alpha\beta$ -Dibromobutyric acid,  $\text{CH}_3\text{-CHBr-CHBr-CO}_2\text{H}$ , was obtained by Körner (*Annalen*, 1866, 137, 234) by the addition of bromine to crotonic acid. Its preparation is described in detail by Michael and Norton (*Amer. Chem. J.*, 1881, 2, 11) and by Kolbe (*J. pr. Chem.*, 1882, [ii], 25, 336). By abstracting hydrogen bromide by means of alkali, Michael and Norton obtained a bromocrotonic acid, melting at  $92^\circ$ , isomeric with the acid, melting at  $106.5^\circ$ , obtained by the same observers from  $\alpha\alpha$ -dibromobutyric acid. Erlenmeyer and Müller (*Ber.*, 1882, 15, 49) showed that when  $\alpha\beta$ -dibromobutyric acid was decomposed with two equivalents of alcoholic potassium hydroxide, a mixture of the two bromocrotonic acids is obtained. These were separated by taking advantage of the great difference in the solubility of their potassium salts in absolute alcohol, when about 10 per cent. of the acid melting at  $106.5^\circ$  was obtained. Wislicenus (*Annalen*, 1888, 248, 322), who described both acids as  $\alpha$ -bromocrotonic acids, used aqueous potassium hydroxide for the decomposition, and obtained a large proportion of  $\alpha$ -bromoallocrotonic acid, melting at  $92^\circ$ , with a slight amount of  $\beta$ -bromocrotonic acid, melting at  $106.5^\circ$ .

Michael and Schulthess (*J. pr. Chem.*, 1892, [ii], 46, 257) confirm the results obtained by Wislicenus, and give quantitative data. Two experiments are described, wherein 10 grams of  $\alpha\beta$ -dibromobutyric acid were decomposed with two equivalents of aqueous potassium hydroxide, one carried out at low temperature ( $0$ – $10^\circ$ ) and the other at  $35^\circ$ . Separating the products by crystallising their potassium salts from ten times their weight of absolute alcohol, they obtained 3.5 per cent. of  $\alpha$ -bromo-salt and 96.5 per cent. of  $\alpha$ -bromoallo-salt in each case.

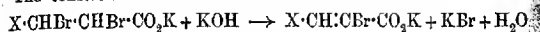
It has been shown by Sudborough and Thompson (*Trans.*, 1903, 88, 671) and by Michael (*Ber.*, 1901, 34, 3666) that the replacement of the acidic hydrogen of  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid by alkyl groups has a profound effect on the decomposition by means of alkalis, the yield of  $\alpha$ -bromocinnamic acid being greatly increased in the case of all the esters used. Michael and Browne (*Amer. Chem. J.*, 1887, 9, 280) state that a similar effect is noticed when the ethyl ester of  $\alpha\beta$ -dibromobutyric acid is similarly decomposed, but the results given in this paper indicate that the effect is not so marked as stated by them.

The experimental work described in this paper may be classified under the following heads:

- I. Determination of the rate of decomposition of certain αβ-dibromo-acids by aqueous potassium hydroxide.
- II. The action of bases on αβ-dibromobutyric acid under varying conditions.
- III. The preparation of esters of αβ-dibromobutyric acid.
- IV. Decomposition of the esters by potassium hydroxide.

I.—The Rate of Decomposition of certain αβ-Dibromo-acids by Aqueous Potassium Hydroxide.

The constants of the reactions



(X=H, CH<sub>3</sub>, or C<sub>6</sub>H<sub>5</sub>) have been determined in aqueous solution at 15°. The general method was to treat a weighed quantity of the finely powdered acid very gradually with one equivalent of pure aqueous potassium hydroxide solution. This was made up to a known volume, and, after being kept for some time in a thermostat at 15°, a second equivalent of alkali was added. Known volumes of the mixture were titrated at definite intervals with standard sulphuric acid.

i. *Dibromopropionic Acid*, CH<sub>3</sub>Br·CHBr·CO<sub>2</sub>H.—This acid was prepared from allyl alcohol, as described by Tollens and Münder, etc. (*Annalen*, 1873, 167, 224, 241). After crystallising from light petroleum, it melts at 63–64°.

*Series A.*—Initial concentration of reacting substances, N/40; 80 c.c. were titrated at intervals with 0·0969N-sulphuric acid  $a=20\cdot65$  c.c.

* Time in hours.	$a-x$ .	$x$ .	$k=1/t \frac{x}{a(a-x)}$ .
0·417	8·55	12·10	0·1645
0·583	7·10	13·55	0·1602
0·917	5·00	15·65	0·1653
2·00	2·70	17·95	0·1610
		Mean.....	0·1627

$$\text{For } N\text{-solution, } k=0\cdot1627 \times \frac{80}{0\cdot0969}=134\cdot4$$

*Series B.*—Initial concentration of the reacting substances, N/50; 20 c.c. were titrated at intervals with 0·01211N-sulphuric acid.  $a=29\cdot50$  c.c.

Time in hours.	$a-x$ .	$x$ .	$k$ .
0·383	16·50	13·00	0·08080
0·533	9·80	19·70	0·08180
		Mean.....	0·08130

$$\text{For } N\text{-solution, } k=0\cdot0813 \times \frac{20}{0\cdot01211}=134\cdot2$$

Mean of Series A and B=134·3

ii.  $\alpha\beta$ -Dibromobutyric Acid.—This acid was prepared as described by Michael (*loc. cit.*), and, after crystallising from carbon disulphide, melted at  $87^\circ$ .

Series A.—Initial concentration of the reacting substances,  $N/8$  approx.; 20 c.c. were titrated at intervals with  $0.0969N$ -sulphuric acid.  $a=24.32$  c.c.

Time in hours.	$a-x$	$x$	$k=1/L \cdot \frac{x}{a(a-x)}$
1.00	17.00	7.32	0.1770
1.53	14.60	9.72	0.1789
2.00	12.95	11.37	0.1805
3.33	9.80	14.52	0.1830
6.00	6.80	17.52	0.1785
7.50	5.75	18.57	0.1770
Mean .....			0.1788

$$\text{For } N\text{-solution, } k=0.1788 \times \frac{20}{0.0969}=3.69$$

Series B.—Initial concentration of reacting substances,  $N/10$  approx.; 20 c.c. were titrated at intervals with  $0.0969N$ -acid.  $a=19.60$  c.c.

Time in hours.	$a-x$	$x$	$k$
0.5	16.80	2.80	0.01700
2.0	11.79	7.81	0.01690
3.0	9.86	9.74	0.01680
4.0	8.25	11.35	0.01754
Mean .....			0.01706

$$\text{For } N\text{-solution, } k=0.01706 \times \frac{20}{0.0969}=3.52$$

Mean of Series A and B = 3.60

iii.  $\alpha\beta$ -Dibromo- $\beta$ -phenylpropionic Acid,  $C_6H_5 \cdot CHBr \cdot CHBr \cdot CO_2H$ .—Initial concentration of the reacting substances,  $N/25$  approx.; 50 c.c. of the solution were titrated at intervals with  $0.0969N$ -acid.  $a=19.10$  c.c.

	Time in hours.	$a-x$	$x$	$k=1/L \cdot \frac{x}{a(a-x)}$
(1)	1.083	18.10	1.00	0.00267
(2)	2.50	17.00	2.10	0.00259
(3)	5.00	15.10	4.00	0.00277
(4)	19.00	8.25	10.85	0.00362
(5)	23.00	6.86	12.24	0.00406

Mean of (1), (2), and (3)..... 0.00268

$$\text{For } N\text{-solution, } K=0.00268 \times \frac{50}{0.0969}=1.38$$

In the later stages (4) and (5) the odour of  $\alpha$ -bromostyrene was distinctly observable, indicating partial decomposition, thus accounting for the high values of  $k$ .

From these experiments it is seen that the rate of elimination of hydrogen bromide from  $\alpha\beta$ -dibromo-acids is considerably affected

by the presence of alkyl groups in the  $\beta$ -position, and depends also on the nature of these groups. The ratios of the constants in the above experiments are:

$$H: Me: Ph: : 100: 2.68: 1.03.$$

It is also apparent that the decomposition of  $\alpha\beta$ -dibromopropionic and  $\alpha\beta$ -dibromobutyric acids by means of potassium hydroxide in dilute aqueous solution at  $15^{\circ}$  is not complicated by side-reactions.

## II.—The Action of Bases on $\alpha\beta$ -Dibromobutyric Acid under Varying Conditions.

A series of experiments has been performed with the view of ascertaining the variation in the proportion of the two  $\alpha$ -bromocrotonic acids obtained by abstracting hydrogen bromide from  $\alpha\beta$ -dibromobutyric acid with different bases under varying conditions. The acid is obtained in theoretical yield by the method described by Michael and by Kolbe, which consists in adding a slight excess of bromine to crotonic acid dissolved in carbon disulphide, keeping for several hours, and then evaporating off the solvent. On crystallising from carbon disulphide or light petroleum, the pure acid, melting at  $87^{\circ}$ , is obtained.

As mentioned above, quantitative results for the action of alcoholic and aqueous potassium hydroxide have been given by Erlenmeyer and Müller and by Michael and Schulthess. Working in alcoholic solution, the former obtained 10 per cent. of  $\alpha$ -bromocrotonic acid, whilst, in aqueous solution, the latter only obtained 3.5 per cent. of this product. Both results are confirmed in the present paper.

The method of separation of the isomerides, as described by Michael and Schulthess, has been tested as follows: 2 grams of  $\alpha$ -bromocrotonic acid and a similar weight of  $\alpha$ -bromo $\alpha$ crotonic acid were mixed and dissolved in 40 grams of absolute alcohol (99.8 per cent.). The solution was titrated with a 10 per cent. solution of alcoholic potassium hydroxide until neutral, and kept in a dark cupboard for two hours, by which time a copious separation of potassium  $\alpha$ -bromocrotonate had occurred. The precipitate was collected on to a weighed filter, washed five times with small quantities of alcohol, and dried in a steam-oven to constant weight, which was 2.48 grams (theory, 2.46 grams). The filtrate was evaporated to dryness, and the residue of potassium  $\alpha$ -bromo $\alpha$ crotonate weighed 2.45 grams. The separation is therefore complete within 1 per cent.

In studying the action of bases on  $\alpha\beta$ -dibromobutyric acid, the general method has been to act on 10 grams of the acid with two molecular proportions of the base until the reaction is completed.

When alcoholic solutions were used, the reaction mixture was then evaporated on a water-bath to remove alcohol, acidified with dilute hydrochloric acid, and extracted five times with ether. After drying, the ethereal solution was evaporated in a vacuum desiccator to constant weight, and the yield of  $\alpha$ -hromo-acids noted. The latter were then dissolved in ten times their weight of absolute alcohol, and titrated with a 10 per cent. solution of alcoholic potassium hydroxide, until neutral. After being kept for two to three hours in the dark, the very sparingly soluble potassium  $\alpha$ -hromocrotonate was collected on a weighed filter, washed several times with small quantities of absolute alcohol, dried in a steam oven, and weighed. The filtrate was evaporated on a steam-bath, dried to constant weight in the steam-oven, and the weight of potassium  $\alpha$ -hromo $\alpha$ llocrotonate determined. In a few cases the latter was determined by difference.

The results for the alkalis used, expressed as percentage yields of the acids obtained, are given in the following table:

Ten grams of  $\alpha\beta$ -dibromohutyric acid treated with two equivalents of alkali (strength approx. normal except where otherwise stated).

Alkali.	Conditions.	Per cent. yield of $\alpha$ -hromo- crotonic acid.	Per cent. yield of $\alpha$ -hromo- $\alpha$ llocrotonic acid.	Total yield.
Potassium hydroxide, aqueous	10—15° for 24 hours	3.35	92.15	95.50
" " "	15 min. on gently boiling water-bath	6.54	88.60	95.15
" " " alcoholic	10—15° for 24 hours	9.45	88.55	98.00
Sodium hydroxide, aqueous...	10—15° for 3 days...	8.50	87.50	96.00
" " " "	" " " "	10.40	85.60	97.00
" " " "	20 min. on gently boiling water-bath	6.55	87.45	95.00
" " " "	20 min. on gently boiling water-bath	7.03	85.77	92.80
Ammonia, aqueous 3 <i>N</i> .....	10—15° for 12 days	Decomposition	incomplete	
" " " ".....	" " " " 6 weeks	21.60	59.90	81.50
" " " ".....	50—60° for 6 hours	4.80	50.70	55.50
" " " ".....	40—50° " 6 "	7.90	53.00	60.90
Ammonia in methyl-alcoholic solution, 3 <i>N</i> .	4 months at ordinary temperature .....	Decomposition	incomplete	
	15 min. on boiling water-bath .....	8.10	51.90	60.00

The  $\alpha$ -hromo- and  $\alpha$ -hromo $\alpha$ llo-crotonic acids were recovered from the potassium salts in each case, and, after recrystallising once from water, melted at 106—107° and 92° respectively.

Experiments were also carried out with the following tertiary bases and alkaloids.

*Trimethylamine*.—Eight grams of  $\alpha\beta$ -dibromohutyric acid were treated with 4.0 grams of trimethylamine (two equivalents) in 25 c.c. of methyl alcohol, a rise of temperature taking place on

mixing. After a week the mixture was worked up as described above, and yielded an 84 per cent. yield of α-bromocrotonic acids, consisting of 45 per cent. of α-bromo- and 39 per cent. of α-bromo-*allo*-acid.

The remaining experiments were carried out with absolute ethyl alcohol as solvent. Ten grams of αβ-dibromobutyric acid were treated with a solution of two equivalents of the base in 50 or 100 c.c. of alcohol, and warmed in a reflux apparatus over a gently boiling water-bath for a definite time. The alcohol was then evaporated off, and the products worked up as usual. The results are given in the following table:

Base.	Volume of solvent, in c.c.	Time of heating, in hours.	Per cent. of α-bromo-acid.	Per cent. of α-bromo- <i>allo</i> -acid.	Per cent. of total yield.
Dimethylaniline ...	100	1	21.2	45.5 *	70.0
" .....	50	1	22.5	74.5	97.0
Pyridine .....	50	1½	16.7	65.2	81.9
" .....	50	1	20.5	71.0	91.5
Quinoline .....	50	1	12.7	63.3	76.0
Brucine .....	100	1½	18.9	29.3 *	50.7
" .....	100	1	25.5	34.0 *	60.5
" .....	100	¾	34.5	32.0	66.5
" .....	100	½	Decomposition incomplete		
Cinchonidine .....	100	1	—	—	64.8
" .....	100	¾	9.7	60.7	70.4
Quinine .....	100	¾	10.9	53.2	64.1

\* Slight loss in these cases.

Control experiments carried out with dimethylaniline showed that neither α-hromocrotonic acid nor α-hromo*allo*crotonic acid is transformed into its isomeride under the conditions of the experiment. Two grams of each acid were separately warmed with two equivalents of the base in alcohol solution for an hour. After working up in the usual manner, 1.80 grams and 1.75 grams respectively of the two acids were recovered, and no trace of the isomerides.

It was noticed, however, that when alcoholic solutions of potassium α-bromo*allo*crotonate were kept for extended periods of time, a gradual transformation into the sparingly soluble α-hromocrotonate occurred. Thus, a solution of 2 grams of the *allo*-salt dissolved in 20 grams of absolute alcohol deposited 0.27 gram of the isomeride during the course of three weeks.

No definite conclusions can be drawn from the results obtained, but, considered generally, the yield of α-bromocrotonic acid is greater the weaker the base used for abstracting hydrogen bromide.

### III.—Preparation of Esters of αβ-Dibromobutyric Acid.

*Ethyl Ester.*—Michael and Browne (*loc. cit.*) describe the preparation of the ethyl ester, which was obtained by saturating a

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solution of one part of the acid in three parts of absolute alcohol with dry hydrogen chloride, the solution being cooled to  $0^{\circ}$ . After twenty-four hours, the liquid was poured into water and extracted with ether, the ethereal solution shaken with sodium carbonate solution, and dried over calcium chloride. By distillation under diminished pressure, they obtained a heavy oil, boiling at  $13-114^{\circ}/30$  mm.

This preparation has been repeated three times, using 20 grams of acid for each experiment, and keeping the mixture for three days. In each case a 60 per cent. yield of ester, consisting of a heavy, colourless liquid, boiling at  $123-124^{\circ}/30$  mm., was obtained. Found, Br=58.35. Calc., Br=58.40 per cent.)

*Methyl Ester.*—This ester was obtained by a method similar to the above; it is a colourless liquid, boiling at  $103^{\circ}/15$  mm. and  $25^{\circ}/48$  mm. It was analysed by Stepanow's method:

0.2926 required 22.56N/10-AgNO<sub>3</sub>. Br=61.59.

C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>Br<sub>2</sub> requires Br=61.49 per cent.

*Allyl Ester.*—This was prepared by dissolving 20 grams of the acid in 50 grams of allyl alcohol, and saturating the solution with dry hydrogen chloride at  $0^{\circ}$ . After three weeks the lower layer of ester was separated, dissolved in ether, washed with dilute sodium carbonate solution and with water, and dried. The ether was removed, and the ester distilled under diminished pressure. A 65 per cent. yield of a colourless, heavy liquid, boiling at  $141.5^{\circ}/0$  mm., was obtained:

0.3795 gave 0.4958 AgBr. Br=55.62.

C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>Br<sub>2</sub> requires Br=55.94 per cent.

#### IV.—Decomposition of the Esters with Potassium Hydroxide.

Michael and Browne (*loc. cit.*) state that when ethyl  $\alpha\beta$ -dibromobutyrate is decomposed with two equivalents of alcoholic potassium hydroxide, warming for a few minutes on a water-bath, the chief product is  $\alpha$ -bromocrotonic acid, the remainder being a small amount of an acid which was not identified. A series of experiments carried out with the esters described above shows that the increase in the relative amount of  $\alpha$ -bromo-acid obtained in this case is not nearly so great as supposed by Michael, and differs greatly in this respect from the analogous decomposition of cinnamic acid dibromide (compare Sudborough and Thompson, *loc. cit.*).

*Ethyl Ester.*—Ten grams of the ester were dissolved in an equal weight of absolute alcohol, and treated with two equivalents of 10 per cent. alcoholic potassium hydroxide. After being kept overnight at  $10-15^{\circ}$ , the alcohol was evaporated off, the acids precipitated with dilute hydrochloric acid, extracted with ether, and

separated as previously described. Three experiments were performed:

	$\alpha$ -Bromo-acid, per cent.	$\alpha$ -Bromo $\alpha$ - <i>llo</i> -acid, per cent.	Total yield, per cent.
(1)	17.6	74.6	92.2
(2)	20.7	79.3	100.0
(3)	20.3	76.7	97.0

*Methyl Ester*.—Three experiments were carried out under similar conditions to the above, using methyl-alcoholic potassium hydroxide. The total yields of product were respectively 95.8, 100, and 100 per cent., the crude acid melting in each case at 89—90°. When separation was attempted in the usual manner, no trace of potassium  $\alpha$ -bromocrotonate separated out after keeping for three hours. The product therefore consists entirely of *allo*-acid.

*Allyl Ester*.—One experiment was performed, in which 10 grams of the ester were dissolved in acetone, and then treated with two equivalents of aqueous potassium hydroxide, sufficient acetone being added to render the solution homogeneous. After keeping overnight, the acetone was evaporated off, and the solution acidified, the acids being extracted and separated as usual. A total yield of 88.9 per cent. of the mixed acids was obtained, consisting of 14.4 per cent. of  $\alpha$ -bromocrotonic acid and 74.5 per cent. of  $\alpha$ -bromo-*allo*crotonic acid.

The author is indebted to Dr. J. J. Sudborough for his advice and interest in this research.

THE EDWARD DAVIES CHEMICAL LABORATORIES,  
ABERYSTWYTH.

## CXLVI.—Freezing-point Curve for Mixtures of Camphor and Phenol.

By JOHN KERFOOT WOOD and JANET DRUMMOND SCOTT.

PHARMACOLOGISTS are well acquainted with the fact that when a small amount of camphor is added to phenol, the mixture assumes the liquid state, and remains in that condition even when cooled to temperatures considerably below the freezing point of phenol. This liquefaction might simply be due to the camphor dissolving in the phenol, thereby lowering the freezing point of the latter; a second reason for the liquefaction might be the formation of a compound of the two substances, the freezing point of the compound being lower than that of phenol. Léger (*Compt. rend.*,



1890, 111, 109) has stated that phenol and camphor unite to form two compounds, a monecamphoride melting at  $-23^{\circ}$  and a hemi-camphoride which remained in the liquid state even when cooled to  $-50^{\circ}$ . Should these statements be correct, the liquefaction which succeeds the addition of camphor to phenol is easily explained. A reference to Léger's paper will show, however, that these conclusions were drawn from what, according to modern physico-chemical ideas, would be regarded as very slight and insufficient experimental evidence. This fact, coupled with the natural interest of the subject, and the additional fact that statements of Léger's relating to mixtures of camphor with the naphthols and other phenolic substances have recently been disproved by Caille (*Compt. rend.*, 1909, 148, 1458), led the authors to re-investigate the subject.

In any such investigation, trustworthy results can only be obtained by examining the behaviour of a large number of mixtures containing the two components in varying proportions. By constructing, therefore, the complete freezing-point curve for all mixtures ranging from pure phenol on the one hand to pure camphor on the other, it will be possible to say, from the form of the curve, whether compounds of phenol and camphor are produced or not when the two substances are mixed.

The phenol used for the experiments was obtained from Kahlbaum, and was freed by distillation from any small amount of water which it might contain. The camphor was the best Japan variety. The results obtained from determinations of the melting points showed both substances to be quite pure.

Suitable amounts of the two substances were weighed into a large test-tube, and were completely mixed by melting them together. The tube was then surrounded by a wider one, thus forming an air jacket, and the whole placed in a vessel filled with a suitable cooling medium. For the mixtures which contained only small amounts of camphor, water formed a suitable cooling agent, whilst in the case of mixtures in which only small quantities of phenol were present, the outer vessel was filled with hot mineral oil. For the cooling of the other mixtures, mixtures of ice and salt or of alcohol and solid carbon dioxide were employed. Uniformity of temperature in the mixture undergoing examination was secured in most cases by means of a mechanical stirring arrangement; with some of the mixtures stirring was difficult, because of the great viscosity of the mixture. Various thermometers were used to indicate the freezing point of the mixtures, a pentane thermometer being used to record the lowest temperatures. The different thermometers were compared with one another, and a table of

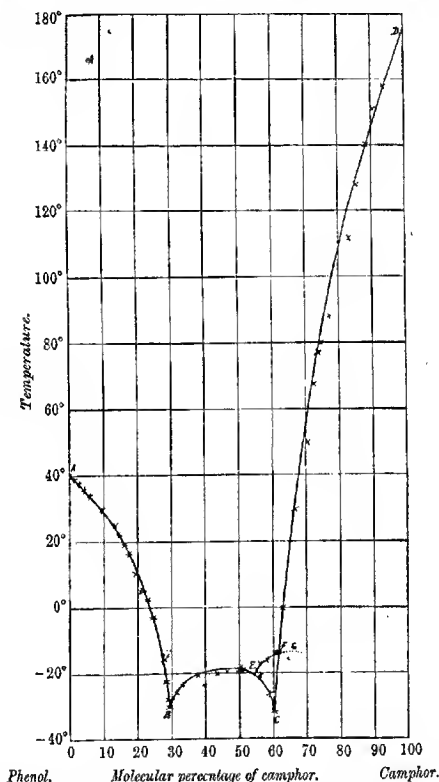
corrections compiled, by means of which the readings given by different instruments could be made comparable. The commencement of freezing was quite apparent in the case of the mixtures containing small amounts of camphor, but with all other kinds of mixtures the most satisfactory way to detect the freezing point was found to be to measure the rate of cooling of the mixture, and note the point at which that rate changed. \* The change in the rate of cooling was in some cases of small dimensions, thus making it a matter of some difficulty to accurately determine the freezing point. It may also be mentioned that with those mixtures which contained large amounts of camphor, it was difficult to see when the camphor began to separate, owing to the refractive indices of the liquid and the solid being very nearly equal. On account of these difficulties, coupled with the difficulty of stirring already mentioned, many of the temperatures given in the table of results may be subject to an error which may amount to 1°. Several determinations of the freezing point were, as a rule, made with each mixture, the results of the different experiments being, for the most part, in close agreement when due allowance is made for the above-mentioned experimental difficulties.

In order to prevent the mixture from being too greatly under-cooled, the consequence of which would, in all probability, be the

TABLE OF RESULTS.

Percentage of camphor in mixture.	Molecular percentage of camphor.	Freezing point.	Percentage of camphor in mixture.	Molecular percentage of camphor.	Freezing point.
0.00	0.00	40.3	61.51	49.71	-20.1
2.32	1.44	39.0	62.21	50.46	-18.7
4.53	2.85	37.5	64.12	51.22	-10.0
6.87	4.36	36.1	66.64	55.23	-19.3
9.42	6.04	34.2	67.53	56.27	-16.7
14.86	9.75	-29.7	67.74	56.48	-20.1
20.31	13.61	25.0	69.32	58.29	-15.9
21.64	14.59	22.0			-26.4
24.10	16.42	19.0	70.12	59.21	-32.0
25.40	17.40	16.1	71.48	60.78	-13.8
28.52	19.79	10.5	72.24	61.67	-13.5
28.92	20.10	7.9	73.37	63.02	-0.1
30.31	21.19	5.0	76.58	66.91	29.5
32.64	23.05	2.4	79.73	70.87	50.7
34.50	24.67	-3.0	81.07	72.59	67.5
38.57	27.97	-15.7	82.19	74.06	77.0
39.52	28.78	-22.5	82.88	74.96	80.0
40.35	29.50	-28.0	84.72	77.43	88.0
42.43	31.31	-30.5	88.85	83.14	112.0
44.90	33.51	-25.7	90.85	85.69	128.0
49.99	38.19	-23.6	92.55	88.47	140.0
52.52	39.88	-20.4	94.06	90.72	151.0
55.80	43.84	-22.6	95.98	93.65	158.0
58.73	46.80	-20.0	100.00	100.00	174.5
		-19.0			

obtaining of too low values for the freezing points, the mixture was inoculated at a temperature near to that at which freezing was expected to take place with small amounts of phenol or camphor, according to which substance was separating out during freezing. The identity of the substance separating from any given



mixture was established by filtering off a portion of the solid and, after thoroughly draining on porous tile, determining its melting point.

The curve showing the relation between the composition of the mixture and the freezing point is shown in the accompanying figure. It will be observed that the curve is made up of three

distinct portions, namely,  $AB$ ,  $BC$ , and  $CD$ ; this fact indicates that the phenol and camphor actually combine to form a compound. The composition of this compound and its limits of stability are most readily seen by plotting, as has been done in the figure, the ratio between the number of molecules of each component in a given mixture instead of the relative weights of the two substances. On referring to the figure, it will be seen that the portion  $BC$ , which corresponds with the compound, reaches its greatest altitude at a point which corresponds with a molecular percentage of camphor of 50. Now the highest point of such a curve indicates the composition and freezing point of the pure compound; at this point the solid which separates and the liquid with which it is in contact have the same composition. It is obvious, therefore, that in the case of the compound of phenol and camphor, the two simple substances are united in equimolecular proportions, and that the freezing point of the compound is about  $-18.6^{\circ}$ . The results of the authors' experiments confirm, therefore, the statement of Léger as to the existence of a monacamphoride of phenol, while the freezing point of the compound, as found by the authors, is in fairly close agreement with the melting point given by Léger.

When the two components are not present in equimolecular proportions, the freezing point of the mixture is lower than that of the pure compound, and falls towards  $B$  or  $C$  respectively, according as to whether it is phenol or camphor which is in excess. The points  $B$  and  $C$  are eutectic points, and represent the limits of stability of the compound. When the ratio between the molecular proportions of phenol and camphor exceeds that of 70.5:29.5, or falls below that of about 40:60, the compound can no longer exist in equilibrium with the liquid; in the former case, phenol will separate out when the mixture freezes, and in the latter case camphor. The lower freezing point given in the table of results for the mixtures containing molecular percentages of camphor of 29.5 and 59.21 represent the freezing points of the eutectic mixtures.

No indication was obtained by the authors as to the existence of a compound formed by the union of two molecules of phenol with one of camphor, as was stated to be the case by Léger; his statement as to the possibility of cooling the mixture to  $-50^{\circ}$  without freezing taking place is in agreement with some of the authors' observations, they having noticed that mixtures in the neighbourhood of the eutectic point  $B$  can often be greatly supercooled without freezing ensuing.

It will be observed from the curve that two or three of the points in the neighbourhood of the eutectic point  $C$  do not fall on the

curve. It might be considered that these points lie on another curve, shown by the dotted line in the figure; if such were the case it would show the existence of a second compound, the composition of which would be shown by the summit *G* of the curve, that is, a compound of two molecules of camphor with one of phenol. The authors do not take the latter view because of the quite definite eutectic point obtained with the 59.21 per cent. mixture, and because with mixtures having almost the same composition as those which gave the discordant results, figures were obtained which fall naturally on the portion *BC* of the curve. The points in question must therefore be considered as due to errors in the determination of the freezing point, probably arising from one or other of the causes mentioned in the earlier part of the paper.

UNIVERSITY COLLEGE,  
DUNDEE.

## CXLVII.—*Morphological Studies of Benzene Derivatives.* *Part I. Introductory.\**

By HENRY E. ARMSTRONG.

IN this series of communications a description will be given of the results of an inquiry which has been carried on in the laboratory under my charge at the City and Guilds Central Technical College, during many years past, whenever I could secure the assistance of competent workers. A brief reference to the work which gave rise to it is to be found in the *Proceedings* of March 3rd, 1892 (p. 40), under the title, "*The Relative Orienting Effect of Chlorine and Bromine. I.—The Constitution of Parabrom- and Parachlor-anilinesulphonic Acids*" by Henry E. Armstrong and J. F. Briggs.

With the object of ascertaining whether any difference in the orienting influence of the two halogen elements could be detected, we had sulphonated *p*-chlorobromobenzene: the product appeared to be a single substance; the results we obtained on contrasting it with the sulphonic acids prepared from *p*-chlor- and *p*-brom-anilinesulphonic acids respectively also led us to assume that the sulphonic radicle occupied the ortho-position relatively to the chlorine atom.

\* In this and the following paper the authors have not always used the nomenclature adopted by the Publication Committee of the Chemical Society: for example, they prefer "ethyl salt" to "ethyl ester."

In view of the fact that corresponding chloro- and bromo-derivatives differ but very slightly in general behaviour, however, the apparently exclusive attraction of the sulphonic radicle by chlorine rather than by bromine was more than surprising; the subject was therefore made the object of further study.

In 1895, with the assistance of Mr. W. T. Gidden, an exhaustive examination was made of the acids obtained on sulphonating *p*-chlor- and *p*-brom-aniline under various conditions. Mr. Briggs, following the directions given by Claus and Mann (*Annalen*, 1891, 265, 87), had mixed the aniline sulphate with eight times its weight of an acid containing 15 per cent. of anhydride and heated the mixture on the water-bath during four hours. In each case only the *meta*-acid was isolated.\*

Little was known at the time of the *ortho*-acids. Various methods of preparing these were tried. A mixture of *p*-brom-aniline sulphate with a molecular proportion of sulphuric acid (100 per cent. acid) was heated at 200–220° during three hours; the *ortho*-acid only was formed but the yield was very small. Better results were obtained by Limpricht's method—by heating the sulphate at about 200°. At about this time Kreis described a method of preparing the *ortho*-acid (*Annalen*, 1895, 286, 377), which involved heating rapidly, in an open dish, a mixture of *p*-bromacetanilide and an equivalent proportion of ordinary concentrated sulphuric acid until the acetic acid was expelled, then baking the salt in an air-oven at 180°. This method was found to give excellent results and to be equally applicable to *p*-chlor-acetanilide, only the *ortho*-acid being formed.

\* The fact that on heating the sulphate with a large excess of fuming acid it was converted into the *meta*-acid, whilst the *ortho*-acid was produced when only a single molecular proportion of sulphuric acid was used, called for an explanation; it appeared not improbable that the *meta*-acid might have been formed by the conversion of the *ortho*-mono-acid produced at first into an unstable *ortho*-*meta*-disulphonic acid, which was subsequently deprived of its *ortho*-sulphonic radicle. On sulphonation, however, the *ortho*-mono-sulphonic acid gave rise only to a di-*ortho*-disulphonic acid: it was therefore to be supposed that the *ortho*- and *meta*-acids were products of distinctly different operations. This observation led me to institute a general inquiry into the process of sulphonation: of this only brief accounts have been published (compare *Proc.*, 1900, 16, 159; *Brit. Assoc. Report*, Dover, 1899, p. 683). I hope

\* Later observations show that, on sulphonating *p*-chlor- and *p*-brom-acetanilide with fuming acid, a small proportion of *ortho*-acid is also formed; whether this be the case when the sulphate is used is now being ascertained.

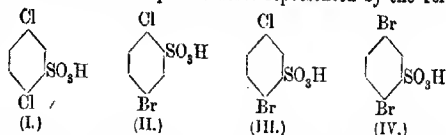
to bring the work under the notice of the Society at an early date, partly in connexion with the chemical side of the inquiry now under consideration and in further discussion of the "laws" which govern substitution in benzenoid compounds.

Two isomeric *p*-chlorobromobenzenesulphonic acids were obtained from the two isomeric *p*-chloraniline- and also from the *p*-bromaniline-*o*- and -*m*-sulphonic acids, corresponding pairs of the amino-acids yielding isomeric acids when the amino-radicle was displaced by halogen. The sulphonic chloride of the one chlorobromosulphonic acid melted at 66°, that of the other at 46°; mixtures of the two melted at intermediate temperatures, the melting point varying as the composition of the mixture was varied according to a linear law: the behaviour of the two compounds, in fact, was in all respects that of isomorphous substances.

The product obtained on sulphonating *p*-chlorobromobenzene gave a sulphonic chloride melting at about the temperature of a mixture of equal proportions of the two sulphonic chlorides; numerous attempts were made to separate the two acids of which it undoubtedly consisted by fractionally crystallising various salts and other derivatives but these were all unsuccessful.

The mistake Mr. Briggs and I had made in assuming that only a single acid was formed was admitted in a note communicated to the British Association at Dover in 1899 (*Report*, p. 627).

I determined to extend the inquiry on the crystallographic side, with the help of Mr. Gidden, to the complete series of sulphonic chlorides and bromides derivable from the *p*-dichloro-, *p*-dibromo- and *p*-chlorobromo-benzenesulphonic acids represented by the formula:



We were able to prepare five of the eight allied compounds in measurable form but were unable to obtain satisfactory crystals of the chloride of both I and III and did not succeed even in preparing the bromide of the latter. The five compounds measured proved to be strictly isomorphous and no indication of polymorphism was observed during their examination; it was found, however, that the ethylic salt prepared from II stood in close morphotropic relationship with the chlorides but was not isomorphous with them. The chlorides and bromides all crystallised in the monosymmetric system, the ethylic salt in the orthorhombic. The following data obtained at this time show how small were the differences observed between the various compounds and par-

icularly that less alteration in crystalline form is involved in the change from sulphonic chloride to bromide than is produced by substituting chlorine for bromine in the benzene nucleus.

*Geometrical Constants.*

	Axial ratios.	Angle.	Angle 110 : 110.
Cl : Br : SO <sub>2</sub> Cl = 1 : 4 : 2	1.1778 : 1 : 2.6216	108° 44' 23"	96° 15'
Cl : Br : SO <sub>2</sub> Br = 1 : 4 : 2	1.1708 : 1 : 2.6250	107 35 21	96 17
Br : Br : SO <sub>2</sub> Cl = 1 : 4 : 2	1.1456 : 1 : 2.6331	110 20 26	94 6
Br : Br : SO <sub>2</sub> Br = 1 : 4 : 2	1.1516 : 1 : 2.6635	109 6 43	94 50
Cl : Cl : SO <sub>2</sub> Br = 1 : 4 : 2	1.1664 : 1 : 2.5861	107 47 42	96 0

In communicating our results to the British Association at Dover (1899), I stated that I had formed the plan of extending the inquiry to the 1:3- and 1:2-derivatives of benzene containing halogens. I was able to announce that Dr. E. C. Jee had already measured the compounds of the 1:3:4-series and had discovered that they formed a remarkable *isotrimorphous* group bearing no apparent relationship to the para-series.

The following year (1900) at Bradford, it was stated in the First Report of the Committee on Isomorphous Derivatives of Benzene (p. 167) that the series included anorthic, orthorhombic and monosymmetric terms, as shown in the following table:

No.	Orientation.			Crystallographic system.		
	1.	3.	4.	Anorthic.	Orthorhombic.	Monosymmetric.
1	Cl	Cl	SO <sub>2</sub> Br	stable		
2	Cl	Br	SO <sub>2</sub> Br	stable		
3	Br	Cl	SO <sub>2</sub> Br	stable		
4	Br	Br	SO <sub>2</sub> Br	labile	→ stable	
5	Br	Br	SO <sub>2</sub> Cl	(labile)	→ stable	labile
6	Br	Cl	SO <sub>2</sub> Cl		stable	labile
7	Cl	Br	SO <sub>2</sub> Cl		labile	→ stable
8	Cl	Cl	SO <sub>2</sub> Cl		labile	→ stable

Of these eight substances, it was pointed out, three are stable in the anorthic system, three in the orthorhombic system and two in the monosymmetric system. Change of the one form into the other had been observed in four cases (4, 5, 7, 8) on allowing the fused substance to cool on a microscopic slide, the direction of the change in each case being that indicated in the table by an arrow. A labile anorthic form of dibromobenzenesulphonic bromide (4) had been crystallised out from solution; moreover, it had been found that each of the four sulphonic chlorides (5—8) can be caused to crystallise in the alternative system by admixture with a sulphonic chloride which usually separates in that system. It had been possible to determine the symmetry of all the forms referred to in the table by crystallographic measurement, with the single



exception of the labile anorthic form of dibromobenzenesulphonic chloride but the existence of this form was indicated by the dimorphous change which occurs on cooling from the melting point to atmospheric temperature.

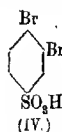
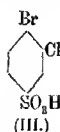
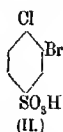
In 1902, at Belfast, I was able to report that Dr. Jee had also practically completed the examination of the second of the three series of 1:3-derivatives (the 1:3:5-sulphonic series) and that these constituted an *isotetramorphous* group, as shown in the following table:

No.	Orientation.			Crystallographic systems.			
	1.	3.	5.	Anorthic.	Mono-symmetric.	Mono-symmetric.	Anorthic.
1	Cl	Cl	SO <sub>3</sub> Br	stable	stable	stable	
2	Cl	Br	SO <sub>3</sub> Br				
3	Br	Br	SO <sub>3</sub> Br		stable	labile	
4	Br	Br	SO <sub>3</sub> Cl			stable	
5	Br	Cl	SO <sub>3</sub> Cl			stable	
6	Cl	Cl	SO <sub>3</sub> Cl				stable

In this series also the dibromobenzenesulphonic bromide is the means of establishing the relationships between the various terms, having been obtained in two distinct forms. But in comparison with the 1:3:4-series, the order of stability is reversed, the transition temperature becoming lower in passing down the series.

The third 1:3(2 sulphonic)-series has given the greatest trouble and up to the present time I have succeeded in obtaining only one of its terms.

In the case of the 1:2-series, five of the eight terms of the 1:2:4-series have been measured by Mr. H. Harding, namely, the chlorides derived from acids I, II and IV and the bromide of II:



Of the chlorides, I and II are practically identical in form; the chloride of IV has been obtained in a distinct form, belonging, however, to the same crystalline system as I. The bromide of II has been obtained in both forms, so that it establishes a connecting link between the two isomorphous series which evidently exist. In this series, the measurements are made with particular difficulty, owing to the low melting points of the compounds and their marked tendency to crystallise in very thin, micaceous plates. Several anilides of this series have been examined and found to exist in two forms.

The difficulties connected with the preparation of the second 1:2-series [the 1:2(3 sulphonic)-derivatives] are not yet overcome.

In planning the inquiry, I hoped that it would be possible eventually to deduce from the data obtained definite conclusions permitting of the correlation of external form with internal molecular structure. The regular relationships discovered in the course of the work served to justify this expectation but there was no obvious mode of discussing the data with such an object in view. I hesitated to publish results which I could not yet interpret in some definite manner. At this juncture the masterly memoir of Barlow and Pope was published, connecting crystalline form with molecular configuration; hope arose in my mind that it would be possible to interpret our data in the light of their views.

It appeared desirable to deal first with the 1:4-series, in which the simplest relationships prevailed between individual members. I was fortunate in securing the assistance of two of my students, Messrs. Colgate and Rodd. With their aid, the earlier work has been revised and the series extended, so as to include the 1:4-iodo- as well as the chloro- and bromo-derivatives and a variety of sulphonates—ethtereal salts and simple and substituted amides—twenty-nine in all. The results at which they have arrived, described in the following memoir, appear to afford clear proof of the existence of a *benzene framework* in all the molecules; it would seem therefore, taking also into account the results previously arrived at by Jerusalem in the case of certain nitro-compounds, that the scheme put forward by Barlow and Pope is one which will embrace the benzenoid compounds generally.

Dr. Jee's and Mr. Harding's measurements of compounds of the 1:3- and 1:2-series will be described and discussed in later communications; the conclusions that can be deduced from them appear to be similar to those arrived at in the case of the 1:4-compounds.

A clue having been found, I hope at no distant date to complete the task which I have undertaken and that it will then be possible to discuss and define the manner in which the superstructure is erected upon the benzene framework. The material collected will also need discussion in other directions.

When the series is completed, if only the sulphonic chlorides and bromides of the dichloro-, dihydro- and bromochloro-benzenes are measured, forty-four different types of compound will have been examined. Thirty of these have been measured already. We shall then have ascertained the angles, so to speak, of almost every possible facet that can be developed on the benzene molecule. If, as appears to be probable, a substructure of benzene be always revealed, what-

ever the nature of the compound, the proof will be complete that the structural elements preserve their individuality in the molecule. To have arrived at such a result will be more than ample reward for the large amount of time and labour spent on the inquiry. Those engaged in the study of constitution have long been satisfied that they are dealing with realities and that the formulae in which they have expressed their conclusions must be given actual value. Structural formulae, however, are as much symbolic of function as of the relative arrangement of the parts; that it should be possible to go further and define the position of these parts in space and the geometrical outcome of their arrangement is a remarkable achievement in which chemists may well take pride.

I would urge in conclusion that the value of crystallography to the chemist should be more fully recognised. The discipline the study affords is in itself of very great value. But it is only right that the chemist should understand and be able to use the language in which alone the crystalline substances he prepares can be described. Analysis is not a means of defining any particular substance; but if crystalline form be determined, a substance is defined for all time and can always be recognised.

The early stages of this work were carried out with the assistance of Mr. Pope, then Instructor of Crystallography in our College; later workers have been aided by Dr. Lowry, his successor. I have to thank both these gentlemen. We are also greatly indebted to Prof. Pope for the aid he has given us in our recent discussion of the data. I have also to acknowledge the help I have received from the Government Grant Fund of the Royal Society and from the British Association.

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CXLVIII.—*Morphological Studies of Benzene Derivatives. Part II. Sulphonic Derivatives of the 1:4-Di-derivatives of Benzene containing Halogens.*

By REGINALD THOMAS COLGATE and ERNEST HARRY RODD.

NINE sulphonic acids of benzene are possible containing two halogen atoms—either chlorine, bromine or iodine—in the para-position in the nucleus; simpler derivatives of all of these have been prepared and have been subjected to careful goniometric examination. The axial ratios and other quantities connected therewith are stated in the table on p. 1590. All the compounds examined crystallise in the monosymmetric system, excepting those numbered 28 and 29, which are orthorhombic.

The nine possible sulphonic chlorides have all been obtained in a form suitable for measurement but several of the corresponding bromides have not yet been isolated, as difficulties attend their preparation; all that have been examined fall into one or other of two crystallographic groups; in each of these groups the individual members have similar geometrical constants and are similar in habit and general crystalline form. The first group includes the substances numbered 1 to 12 in the table; the second comprises substances 13, 14 and 15. It is noteworthy that each series includes one of the isomeric chloridobenzenesulphonic chlorides but that the sulphonic bromide of the 1:4:2-sulphonic acid occurs in the same series as the chloride of the isomeric 1:4:3-acid. This behaviour is an indication of isodimorphism, and on one occasion a crop of crystals of a labile modification of the 1:4-iodochlorobenzene-2-sulphonic chloride was actually obtained: these crystals rapidly became cloudy and opaque after removal from the benzene solution but melted at 70°, the melting point of the stable form. Apparently the labile form can be obtained by suddenly cooling the molten substance, as when thus treated the compound melts at 62°. In the case of 1:4-bromiodobenzene-2-sulphonic chloride, not only was a similar crop of labile crystals obtained but it was found possible to measure it. The result showed clearly that the modification belongs to the first or large group; the stable modification, which we have not yet obtained in measurable form, is presumably a member of the second group.

Although the axial ratios of the members of the two series are widely different, on comparing their equivalence parameters it is obvious that the substances are closely related.\*

\* As defined by Barlow and Pope, the equivalence parameters represent the dimensions of a parallelepipedon the edges of which are parallel with and pro-

Barlow and Pope have shown that two alternative modes exist of close-packing the benzene units or molecules in homogeneous arrangement (Trans., 1906, 89, 1699); these are derived respectively from the hexagonal and the cubic closest-packed arrangement of equal spheres. The former type of arrangement is exhibited in the known orthorhombic modification of benzene, which has the axial ratios  $a:b:c=0.891:1:0.799$ , Barlow and Pope having shown clearly that these constants are obtainable by a slight distortion of the completely hexagonal mode of packing the benzene units; this arrangement is known as the hexagonal marshalling of the benzene units. Calculating from these axial ratios and taking into account the valency volume of the hydrocarbon ( $W=30$ ), the equivalence parameters of this type of marshalling of the benzene assemblage are  $x:y:z=3.101:3.480:2.780$ . These numbers represent translations in the crystalline benzene assemblage in three directions at right angles; on inspection of the Barlow-Pope diagrams, it is obvious that the value  $z=2.780$  is a measure of the height of two links in the column of carbon spheres in the assemblage. Whilst the diagrams represent the  $z$  value as being very slightly less than the sum of the diameters of one carbon and one hydrogen domain, the quantity  $y=3.480$  is twice the diameter of a carbon domain. These quantities refer to dimensions in the assemblage after suppression of the interstitial space. It has been shown by Barlow and Pope and by Jerusalem that the dimension  $z=2.780$  occurs as one of the equivalence parameters in a large number of benzene derivatives which have been crystallographically examined and it has been concluded that when hydrogen atoms in the benzene molecule are displaced by other atoms or radicles, the columns of carbon spheres in the crystalline assemblage referred to above retain their structure intact and are merely moved apart to accommodate the substituting groups.

The alternative mode of close-packing the benzene units in homogeneous assemblage is derived from the cubic closest-packed assemblage of equal spheres; in this type of assemblage the  $z$  dimension must be rather smaller than in that previously considered. As this assemblage presents a rhombohedral form of arrangement, it is termed the rhombohedral marshalling of the benzene units. The marshalling being rhombohedral, crystals affecting this type of structure must be expected to exhibit (a) pseudo-hexagonal symmetry, one of the axial ratios approximating to  $1:1.1547$  or  $1:0.8165$ ; on the other hand,

portional to the crystallographic axes, its volume being numerically equal to the sum of the fundamental valencies of the atoms in the molecule. The equivalence parameters of the substances described are calculated in the case of compounds 1 to 16 from the axial ratios deduced from the actual measurements, no fractional parts of the axial ratios being used.

being derived from the cubic closest-packed assemblage of equal spheres, it may also show (b) pseudo-cubic symmetry. In the case of (a), one of the equivalence parameters should have a value somewhat less than 2.78, whilst in the case of (b) the value somewhat less than 2.788 cannot appear but either two or the three equivalence parameters should be nearly equal.

Jerusalem has shown clearly that the anticipations expressed above, which are summarised from Barlow and Pope's description (*loc. cit.*, p. 1692), are realised in the results obtained by the crystallographic examination of the picrates and styphnates (Jerusalem, *Trans.*, 1909, 95, 1275).

Inspection of the equivalence parameters of the sulphonic chlorides and bromides recorded in the table on p. 1590 shows that with the exception of No. 13 all include a  $z$  value appreciably less than 2.780; the values lie between 2.661 and 2.741, the total variation being about 3 per cent.

Further, in Nos. 1 to 12 the ratio  $c:b$  approximates to the hexagonal ratio of 1.1547:1; in Nos. 13 to 15 the ratio  $a:b$  approximates, although less closely, to the alternative hexagonal ratio of 0.8165:1. There is thus considerable evidence that all these substances are of the rhombohedral type of marshalling, with the possible exception of No. 12, in which the  $z$  value is nearly appropriate to the hexagonal marshalling. The considerable difference between the  $\beta$ -angle for No. 13 and those for Nos. 14 and 15 confirms the suggestion that both types of marshalling occur in the three substances. Another point of interest in connexion with the equivalence parameters is that when it is possible to compare the numbers for corresponding sulphonic chlorides and bromides, as in pairs 1 and 2, 3 and 4, 7 and 8, 10 and 11, the  $y$  parameters are nearly identical; the morphotropic relationship thus displayed, however, is only revealed by the equivalence parameters.

We have determined the axial ratios and equivalence parameters of a considerable number of sulphanilides and sulphotoluidides derived from the chlorides. Most of these substances crystallise far more readily than the chlorides and bromides in measurable form and may therefore be measured accurately with facility. The equivalence parameters deduced for these substances are such that they must be supposed to exhibit one or other of the two kinds of marshalling already discussed.

The anilides and toluidides are in several cases isodimorphous. Pure *p*-dibromobenzenesulphanilide, for example, crystallises from acetone in a labile form; when removed from the solution, the crystals are brilliant and transparent but almost immediately become opaque and the crystal faces dull; the measurement of this compound was

therefore a matter of some difficulty. It appears that the presence of a trace of anilino in the solution always ensures the deposition of the compound in the stable form.




1:4-Chlorobromobenzene-2-sulphanilide is another similar case. Only a few measurements of the labile form of this compound were obtained but judging from these and from the forms appearing on the crystals it is closely isomorphous with the labile form of *p*-dibromobenzenesulphanilide. All the other anilides studied up to the present have been obtained as yet only in a stable form. The following data have been deduced from the measurements made of the anilides:

Orientation.												
	1.	4.	2.	$a : b : c.$	$\beta.$	$x :$	$y :$	$z.$	M. p.			
17	Cl	Br	SO <sub>2</sub> NHPh	1.339 : 1.1058	98° 7'	7.752 :	2.894 :	3.062	138°			
18	Br	Cl	SO <sub>2</sub> NHPh	1.338 : 1.1047	98 30	7.776 :	2.906 :	3.043	164			
19	Br	Br	SO <sub>2</sub> NHPh	1.329 : 1.1025	97 58	7.793 :	2.932 :	3.005	143			
20	I	Cl	SO <sub>2</sub> NHPh	1.350 : 1.0997	97 15	7.943 :	2.942 :	2.933	168			
21	I	Br	SO <sub>2</sub> NHPh	1.329 : 1.0979	97 18	7.909 :	2.976 :	2.913	150			
22	Br	Br	SO <sub>2</sub> NHPh	1.372 : 1.1163	97 50	7.631 :	2.781 :	3.234	143			

The valency volume of the anilides is 68; the parameter values are obtained by multiplying the  $a$  axial ratio value by 28. These anilides evidently constitute a well-defined isomorphous group. The fact that a number approximating to 2.9 occurs twice in each set of equivalence parameters is an indication that in each case the axial directions have been so chosen as to demonstrate the pseudo-cubic nature of the assemblage, a possibility which we have already considered. The property of exhibiting pseudo-cubic symmetry being characteristic of the rhombohedral type of marshalling of benzene units, we conclude that the anilides display that type of marshalling in their crystals. The compound numbered 22 is the labile form of *p*-dibromobenzenesulphanilide. Its crystals evidently display hexagonal marshalling, as the number 2.78 occurs among the parameter values. The labile form of 1:4-chlorobromobenzene-2-sulphanilide (17) we have proved to be isomorphous with (22), although we have not been able to measure it completely.

It is clear from the evidence that the sulphanilides form an isomorphous group of substances, as each of two of the compounds has been obtained in two forms, one stable and the other labile, the two stable forms and the two labile forms being respectively isomorphous. As the stable crystals exhibit rhombohedral and the labile hexagonal marshalling, both types of arrangement characteristic of benzene are represented in this group of compounds.

To contrast the toluidides with the anilides, we have prepared and measured the *o*-, *m*- and *p*-toluidides of 1:4-chlorobromobenzene-2-sulphonic acid and also the *p*-toluidide of *p*-dibromobenzenesulphonic acid. The results obtained are as follows:

1. 4. 2.			$\alpha : b : c.$	$\beta.$	$x : y : z.$	Fractions of ratios. M. p.	
20	Cl	Br 	0.727 : 1 : 1.195	102° 5'	8.122 : 2.792 : 3.262	4a	151°
21	Cl	Br 	0.751 : 1 : 1.154	100.37	8.430 : 2.782 : 3.210	4a	150°
22	Cl	Br 	0.767 : 1 : 0.959	98.25	9.022 : 2.940 : 2.820	4a	157
23	Br	Br	0.764 : 1 : 0.959	98.32	9.001 : 2.943 : 2.824	4a	152

A striking fact is disclosed in these results: the *o*- and *m*-toluidides are obviously derived from the labile anilide, being of hexagonal marshalling, as the presence among the parameters of the number 2.78 indicates; the *p*-toluidide, on the other hand, is clearly derived from the stable anilide, being of rhombohedral marshalling and exhibiting pseudo-cubic symmetry.

The following comparison gives emphasis to these relationships:

$x : y : z.$			$x : y : z.$		
Labile anilide (19)	7.631	: 2.781	: 3.234	Stable anilide (14)	7.752 : 2.894 : 3.062
<i>o</i> -Toluidide (20)	8.122	: 2.792	: 3.262	Stable anilide (16)	7.793 : 2.932 : 3.005
<i>m</i> -Toluidide (21)	8.430	: 2.782	: 3.210	<i>o</i> -Toluidide (22)	9.022 : 2.940 : 2.820
				<i>p</i> -Toluidide (23)	9.001 : 2.943 : 2.824

The greater part of the change of the dimensions conditioned by the introduction of a methyl group in place of an atom of hydrogen occurs in one direction, namely, on the  $x$  parameter.

Indications of dimorphism have been observed in the case of the *o*-toluidide (20). The melting point of crystals separated from acetone is 151°. If the melted substance be suddenly cooled, however, it assumes the vitreous or isotropic state but when gently warmed the solid crystallises in a form which melts at 142—143°.

It is clear from the occurrence of this value 2.78 in the equivalence parameters of the anilides and toluidides that in these compounds the two benzene nuclei must lie in the same plane. Barlow and Pope have shown this to be the case in other compounds containing more than one benzene nucleus, for example, in triphenylmethane.

We have also prepared the methylic and ethylic salts of *p*-dibromobenzenesulphonic acid and the ethylic salt of 1:4-chloriodobenzene-2-sulphonic acid. The two ethylic salts crystallise in the orthorhombic and the methylic in the monosymmetric system. All were obtained in measurable form only after considerable trouble.

The following results were obtained:




Orientation.			$\alpha : b : c.$	W. of ratios.	Fractions			$\beta.$
1.	4.	2.			$x :$	$y :$	$z.$	
Br	Br	SO <sub>3</sub> OMe	2.443 : 1 : 1.167	44	—	5.895	: 2.454 : 2.930	94.0°
Br	Br	SO <sub>3</sub> OEt	1.187 : 1 : 1.065	50	2a	6.455	: 2.697 : 2.872	90.0
I	Cl	SO <sub>3</sub> OEt	1.294 : 1 : 1.114	50	2a	6.697	: 2.589 : 2.833	90.0



The  $y$  parameter values may be regarded as indicating that these compounds are of rhombobedral marshalling, the  $y$  value being somewhat less than the  $z = 2.78$  value characteristic of benzene.

To sum up, it is apparent that all the compounds described in the present communication are of two types, one derived from the hexagonal and the other from the cubic mode of packing equal spheres in the closest possible manner.

It is to be supposed that the carbon atoms in each molecular complex are arranged in almost exactly the same manner as are those in crystalline benzene and that the substituting atoms or groups take the place of the hydrogen atoms they displace by expanding the benzene assemblage in two only of the three possible directions. The orthorhombic symmetry of the benzene assemblage is usually lowered, however, to monosymmetric symmetry, the shear which causes this change taking place in a direction parallel with either plane of symmetry of the orthorhombic assemblage, so that the value 2.78 is found on either the  $y$  or the  $z$  parameter in the monosymmetric derivative; thus in the case of 1:4-chloriodobenzene-2-sulphonic chloride this

	Orientation.			Axial ratios.		W.	Equivalence parameters.			M. p.
	1.	2.	3.	$a : b : c$	$\beta$		$x : y : z$			
1	Cl	SO <sub>2</sub> Cl	Cl	2.470 : 1 : 1.179	97.23	36	5.696 : 2.325 : 2.741		88	
2	Cl	SO <sub>2</sub> Br	Cl	2.439 : 1 : 1.166	98.41	36	5.753 : 2.325 : 2.709		74	
3	Cl	SO <sub>2</sub> Cl	Br	2.509 : 1 : 1.178	97.40	36	5.790 : 2.318 : 2.718		86	
4	Cl	SO <sub>2</sub> Br	Br	2.731 : 1 : 1.171	98.35	36	5.640 : 2.307 : 2.702		110	
5	Br	SO <sub>2</sub> Cl	Cl	2.308 : 1 : 1.133	99.5	36	5.685 : 2.370 : 2.687		46	
6	Br	SO <sub>2</sub> Br	Cl	2.438 : 1 : 1.115	97.45	36	5.735 : 2.352 : 2.693		83	
7	Br	SO <sub>2</sub> Cl	Br	2.476 : 1 : 1.144	95.26	36	5.787 : 2.337 : 2.674		71	
8	Br	SO <sub>2</sub> Br	Br	2.479 : 1 : 1.145	96.49	36	5.796 : 2.338 : 2.676		114	
9	I	SO <sub>2</sub> Br	Cl	2.169 : 1 : 1.154	95.50	36	5.701 : 2.333 : 2.692		102	
10	Cl	SO <sub>2</sub> Cl	I	2.583 : 1 : 1.176	99.7	36	5.914 : 2.289 : 2.692		85	
11	Cl	SO <sub>2</sub> Br	I	2.567 : 1 : 1.167	100.30	36	5.912 : 2.305 : 2.689		143	
12	Br	SO <sub>2</sub> Cl	I	2.555 : 1 : 1.158	94.23	36	5.852 : 2.302 : 2.666		91	
13	I	SO <sub>2</sub> Cl	Cl	0.729 : 1 : 0.654	99.42	36	3.065 : 4.247 : 2.779		79	
14	I	SO <sub>2</sub> Cl	Br	0.815 : 1 : 0.673	95.28	36	3.291 : 4.040 : 2.719		67	
15	I	SO <sub>2</sub> Cl	I	0.885 : 1 : 0.693	95.22	36	3.409 : 3.986 : 2.661		132	
16	Cl	SO <sub>2</sub> NH <sub>2</sub>	Cl	0.433 : 1 : 0.121	91.11	1	2.573 : 6.079 : 2.558		182	
17	Cl	SO <sub>2</sub> NHPh	Br	1.333 : 1 : 1.053	93.7	63	7.552 : 2.894 : 3.062		133	
18	Br	SO <sub>2</sub> NHPh	Cl	1.338 : 1 : 1.047	96.30	64	7.776 : 2.906 : 3.043		164	
19	Br	SO <sub>2</sub> NHPh	Br	1.329 : 1 : 1.045	97.53	63	7.793 : 2.932 : 3.065		143	
20	I	SO <sub>2</sub> NHPh	Cl	1.350 : 1 : 0.997	97.15	65	7.913 : 2.942 : 3.063		163	
21	I	SO <sub>2</sub> NHPh	Br	1.339 : 1 : 0.979	97.18	68	7.909 : 2.972 : 3.013		150	
*22	Br	SO <sub>2</sub> NHPh	Br	1.372 : 1 : 1.163	97.50	68	7.681 : 2.781 : 3.234		143	
23	Cl	SO <sub>2</sub> NH- 	Br	0.727 : 1 : 1.195	102.5	74	8.123 : 2.792 : 3.262		151	
24	Cl	SO <sub>2</sub> NH- 	Br	0.751 : 1 : 1.154	100.37	74	8.430 : 2.782 : 3.210		159	
25	Cl	SO <sub>2</sub> NH- 	Br	0.767 : 1 : 0.939	93.25	74	9.022 : 2.940 : 3.320		157	
26	Br	SO <sub>2</sub> NH-	Br	0.764 : 1 : 0.959	95.32	71	9.001 : 2.943 : 3.324		152	
27	Br	SO <sub>2</sub> Me	Br	2.443 : 1 : 1.107	94.0	44	6.995 : 2.454 : 2.950		63	
28	Br	SO <sub>2</sub> Et	Br	1.197 : 1 : 1.055	99.0	50	6.455 : 2.697 : 2.972		86	
*29	I	SO <sub>2</sub> Et	Cl	1.294 : 1 : 1.114	99.0	50	6.697 : 2.689 : 2.933		88	

\* Labile form.

number is found on the  $z$  parameter, whilst in that of the labile  $p$ -dichlorobenzenesulphanilide it occurs on the  $y$  parameter.

The halogen atoms appear to displace one another in the molecule without producing more than a slight change in the relative dimensions of the structure.

The preceding is a complete list of the compounds described:

### 1. *p*-Dichlorobenzenesulphonic Chloride.

Great difficulty was experienced in obtaining this substance in measurable crystals. Until highly purified, it did not crystallise at all, the solution solidifying as a whole when very concentrated. Measurable crystals (m. p.  $38^{\circ}$ ) were at length obtained from a solution in benzene kept at the temperature of melting ice. [Found, (sulphonic) Cl = 14.43. Calc., Cl = 14.46 per cent.]

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.450:1:1.179$ ;  $\beta = 97^{\circ}25'$ .

Equivalence Parameters:  $x:y:z = 5.636:2.325:2.741$ .

Forms observed:  $\{100\}$ ,  $\{111\}$ ,  $\{001\}$ ,  $\{110\}$ ,  $\{1\bar{1}1\}$ ,  $\{2\bar{2}1\}$ .

The following measurements were made:

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 110	19	$67^{\circ}22' - 67^{\circ}53'$	$67^{\circ}38'$	—
110 : 110	9	$44^{\circ}35' - 45^{\circ}3'$	$44^{\circ}45'$	$44^{\circ}44'$
100 : 111	15	$76^{\circ}35' - 77^{\circ}33'$	$77^{\circ}5'$	—
111 : $\bar{1}\bar{1}1$	8	$34^{\circ}9' - 35^{\circ}8'$	$34^{\circ}34'$	$34^{\circ}37'$
$\bar{1}\bar{1}1$ : 100	7	$68^{\circ}18' - 68^{\circ}23'$	$68^{\circ}19'$	$68^{\circ}18'$
001 : 111	6	$53^{\circ}11' - 53^{\circ}25'$	$53^{\circ}16'$	$53^{\circ}23'$
111 : 110	2	$39^{\circ}14' - 39^{\circ}35'$	$39^{\circ}23'$	$39^{\circ}26'$
001 : $\bar{1}\bar{1}1$	2	$49^{\circ}47'$	$49^{\circ}47'$	$49^{\circ}56'$
100 : 001	5	$97^{\circ}22' - 97^{\circ}28'$	$97^{\circ}25'$	—
001 : 100	5	$82^{\circ}30' - 82^{\circ}34'$	$82^{\circ}33'$	$82^{\circ}34'$
111 : $\bar{1}\bar{1}1$	2	$95^{\circ}47' - 95^{\circ}51'$	$95^{\circ}49'$	$96^{\circ}2'$

### 2. *p*-Dichlorobenzenesulphonic Bromide.

This substance was prepared and measured by Gidden. The axial ratios given by him were recalculated for a different value of  $\beta$ . His data with corrected indices for the faces are given below. Melting point  $74^{\circ}$ :

Axial Ratios:  $a:b:c = 2.490:1:1.166$ ;  $\beta = 98^{\circ}41'$ .

Equivalence Parameters:  $x:y:z = 5.785:2.323:2.709$ .

Angle.	No. of observations.	Mean.	Calculated.
111 : $\bar{1}\bar{1}1$	41	$96^{\circ}0'$	—
100 : 111	63	$78^{\circ}12'$	—
100 : 001	10	$81^{\circ}19'$	—
111 : 001	10	$53^{\circ}14'$	$53^{\circ}12'$
100 : 110	4	$67^{\circ}53'$	$67^{\circ}54'$
111 : $\bar{1}\bar{1}0$	2	$52^{\circ}20'$	$52^{\circ}18'$

## 5. 1:4-Bromochlorobenzene-2-sulphonic Chloride.

In preparing this compound, even more difficulty was experienced in crystallising it than in the case of *p*-dichlorobenzenesulphonic chloride. From benzene or a mixture of benzene and light petroleum, it separates in very thin, hexagonal plates melting at  $46^{\circ}$ ; by keeping the solution at  $0^{\circ}$ , thicker crystals are obtained but their laminated structure renders them useless for purposes of measurement; ultimately measurable crystals were obtained from a mixture of benzene with petroleum boiling at  $100-120^{\circ}$ . [Found, (sulphonic) Cl = 12.17,  $C_6H_3O_2Cl_2Br$  requires (sulphonic) Cl = 12.23 per cent.]

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.398:1:1.133$ ;  $\beta = 96^{\circ}5'$ .

Equivalence Parameters:  $x:y:z = 5.685:2.370:2.687$ .

Forms observed:  $\{100\}$ ,  $\{001\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{221\}$ .

The following measurements were made:

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 111	13	$76^{\circ} 5' - 76^{\circ} 38'$	$76^{\circ} 18'$	—
111 : 100	11	$103^{\circ} 27' - 103^{\circ} 51'$	$103^{\circ} 41'$	$103^{\circ} 42'$
100 : 001	11	$95^{\circ} 29' - 96^{\circ} 25'$	$96^{\circ} 1'$	$96^{\circ} 5'$
001 : 100	12	$83^{\circ} 30' - 84^{\circ} 29'$	$83^{\circ} 55'$	—
001 : 111	15	$51^{\circ} 30' - 52^{\circ} 27'$	$52^{\circ} 7'$	—
111 : 110	2	$40^{\circ} 4' - 40^{\circ} 13'$	$40^{\circ} 9'$	$40^{\circ} 15'$
111 : 221	4	$61^{\circ} 43' - 62^{\circ} 19'$	$61^{\circ} 55'$	$61^{\circ} 59'$
221 : 001	2	$65^{\circ} 32' - 65^{\circ} 43'$	$65^{\circ} 40'$	$65^{\circ} 54'$
100 : 221	3	$66^{\circ} 40' - 67^{\circ} 16'$	$66^{\circ} 55'$	$66^{\circ} 54'$

## 6. 1:4-Bromochlorobenzene-2-sulphonic Bromide.

This compound was measured by H. Harding; it melts at  $83^{\circ}$ .

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.4383:1:1.1456$ ;  $\beta = 97^{\circ}45'$ .

Equivalence Parameters:  $x:y:z = 5.735:2.352:2.693$ .

Forms observed:  $\{100\}$ ,  $\{001\}$ ,  $\{111\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 001	8	$82^{\circ} 2' - 82^{\circ} 38'$	$82^{\circ} 15'$	—
100 : 001	5	$97^{\circ} 34' - 97^{\circ} 48'$	$97^{\circ} 45'$	$97^{\circ} 45'$
001 : 111	4	$52^{\circ} 37' - 52^{\circ} 42'$	$52^{\circ} 39'$	$52^{\circ} 38'$
100 : 111	8	$77^{\circ} 14' - 77^{\circ} 33'$	$77^{\circ} 27'$	—
111 : 111	4	$85^{\circ} 14' - 85^{\circ} 23'$	$85^{\circ} 19'$	—

## 18. 1:4-Bromochlorobenzene-2-sulphanilide.

This compound crystallises well from acetone in prisms melting at  $164^{\circ}$ .

System: Monosymmetric.

Axial Ratios:  $a:b:c = 1.047:1:1.338$ ;  $\beta = 98^{\circ}30'$ .

Equivalence Parameters, taking 2a with  $W = 68$ :  $x:y:z = 7.776:2.906:3.043$ .

Forms observed: {100}, {001}, {101}, {10 $\bar{1}$ }, {111}, {11 $\bar{1}$ }, {121}.

The following measurements were made:

Angle.	No. of observations.	Limits.	Mean.	Calculated.
101 : 001	6	40°57'—41°33'	41° 9½'	41°11'
100 : 101	8	56 57 — 57 36	57 20	57 19
100 : 10 $\bar{1}$	9	46 17 — 47 16	46 54	46 45
101 : 00 $\bar{1}$	7	34 17 — 35 25	34 30	34 45
100 : 001	12	98 4 — 98 55	98 29½	98 30
001 : 100	10	81 6 — 81 50	81 30	81 30
100 : 111	25	65 52 — 66 28	66 6	—
111 : 100	23	113 30 — 114 25	113 52	113 54
101 : 111	9	37 3 — 37 47	37 24	37 20
111 : 121	8	18 59 — 19 42	19 20	19 25
101 : 121	15	56 27 — 56 54	56 45	56 45
121 : 121	25	66 21 — 66 38	66 30	—
111 : 11 $\bar{1}$	31	82 22 — 83 24	82 47	—
111 : 11 $\bar{1}$	23	96 50 — 97 35	97 14	97 18
111 : 121	6	48 52 — 49 22	49 9	49 14

A peculiarity of all the crystals of stable forms of the anilides which we have examined is that most erratic readings are generally obtained from the zone {101}, {111}, {121}, etc., namely, the zone around the prism. After examining a large number of crystals, we found that, as a rule, the form {121} is accompanied by another very close to it, the angle between the two varying from 1° to 3°, sometimes one, sometimes the other being absent, however. This explained the erratic readings which had been obtained for the angle 121 : 121. On calculating this angle from readings not involving the erratic zone, we found that the smallest readings of the angle—which were remarkably constant—agreed with the calculated value. The same peculiarity was observed in the case of all the anilides of this series that we examined.

### 3. 1:4-Bromochlorobenzene-3-sulphonic Chloride.

This chloride crystallises with great facility from benzene in rhombs or rhombic plates, melting at 66°. [Found, (sulphonic) Cl = 12.16. Calc., Cl = 12.23 per cent.]

The substance was measured originally by W. T. Gidden. A few measurements which we made agree with his. The axial ratios are calculated from his data.

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.569:1:1.178$ ;  $\beta = 97^\circ 40'$ .Equivalence Parameters:  $x:y:z = 5.790:2.308:2.718$ .

Angle.	No. of observations.	Mean.	Calculated.
111 : $\bar{1}\bar{1}\bar{1}$	59	$96^\circ 15'$	—
100 : 111	81	$77^\circ 37'$	—
100 : $\bar{1}\bar{1}\bar{1}$	23	$63^\circ 23'$	—
$\bar{1}\bar{1}\bar{1}$ : $\bar{1}\bar{1}\bar{1}$	24	$33^\circ 56'$	$33^\circ 55'$
110 : 111	2	$39^\circ 32'$	$39^\circ 34'$
111 : $\bar{1}\bar{1}\bar{1}$	7	$103^\circ 2'$	$103^\circ 4'$
$\bar{2}\bar{2}\bar{1}$ : 111	3	$60^\circ 55'$	$60^\circ 50'$
$\bar{1}\bar{1}\bar{1}$ : $\bar{2}\bar{2}\bar{1}$	7	$16^\circ 5'$	$16^\circ 6'$
$\bar{2}\bar{2}\bar{1}$ : 110	3	$21^\circ 19'$	$21^\circ 16'$

## 4. 1:4-Chlorobromobenzene-2-sulphonic Bromide.

This bromide was measured by Gidden. It crystallises readily from benzene in the usual rhombs (m. p.  $110^\circ$ ) characteristic of these compounds.

System: Monosymmetric.

Axial Ratios, calculated from Gidden's data:  $a:b:c = 2.531:1:1.171$ ;  
 $\beta = 98^\circ 35'$ .

Equivalence Parameters:  $x:y:z = 5.840:2.307:2.702$ .

Angle.	No. of observations.	Mean.	Calculated.
111 : $\bar{1}\bar{1}\bar{1}$	40	$96^\circ 17'$	—
100 : 111	38	$78^\circ 22'$	—
110 : $\bar{1}\bar{1}\bar{1}$	6	$51^\circ 55'$	—
110 : 111	2	$39^\circ 56'$	$39^\circ 58'$
111 : 001	8	$53^\circ 13'$	$53^\circ 12'$
100 : $00\bar{1}$	2	$81^\circ 3'$	$81^\circ 25'$
100 : 110	4	$63^\circ 10'$	$63^\circ 13'$

## 17. 1:4-Chlorobromobenzene-2-sulphanilide.

This affords an example of a dimorphous substance. When pure it crystallises from acetone in a labile form. When the bright crystals are removed from the solution in which they have been formed, they rapidly become opaque and the crystal faces become covered with a fine powder. These crystals are very soft and fall to powder under slight pressure. Owing to the rapidity with which transition from the labile to the stable form takes place, great difficulty is experienced in obtaining measurements of these crystals. A few angles were determined, however, which proved that the crystals are isomorphous with the labile form of *p*-dibromobenzene-sulphanilide, which we were able to measure completely. The habit and forms present also prove this to be the case.

If a small quantity of aniline be present in the acetone solution, the sulphanilide crystallises in a stable form isomorphous with

2-bromo-5-chlorobenzenesulphanilide; thus the labile or stable form can be obtained at will. At times both forms have developed simultaneously in the same solution; this has also been observed to take place in the case of *p*-dibromobenzenesulphanilide. Both forms melt at 138°.

(Stable form).—System: Monosymmetric.

Axial Ratios:  $a:b:c=1.058:1:1.3395$ ;  $\beta=98^{\circ}7'$ .

Equivalence Parameters:  $x:y:z=7.752:2.894:3.062$ . [2a.]

Forms present: {001}, {101}, {101}, {111}, {111}, {121}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
101:001	10	56°33'—57° 8'	56°47'	56°46'
001:101	11	46 38 —46 56	46 45	—
101:101	11	76 9 —76 50	76 29	—
111:101	16	41 14 —41 53	41 28	41 30½
111:111	15	82 46 —83 25	83 1	—
111:111	5	96 40 —97 8	96 57	96 59
111:111	6	56 39 —57 37	56 56	57 6
111:001	5	56 43 —57 40	57 7	57 8
001:111	16	65 33 —66 9	65 43	65 46

### 23. 1. 4-Chlorobromobenzene-2-sulpho-o-toluidide.

This compound crystallises extremely well from acetone; it melts partly at 143—144°, then resolidifies above that temperature and melts sharply at 151°. When suddenly cooled, it assumes the vitreous form; when gently warmed, this crystallises in the form which has the lower melting point, the substance melting completely at 143—144° and not resolidifying. It is evident from this that the form stable at the ordinary temperature is that melting at 143°, which is metastable at its melting point.

System: Monosymmetric.

Axial Ratios:  $a:b:c=0.727:1:1.195$ ;  $\beta=102^{\circ}5'$ .

Equivalence Parameters:  $x:y:z=8.122:2.792:3.262$ . [4a.]

Forms observed: {001}, {010}, {101}, {101}, {011}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
001:101	12	67°30'—68° 8'	67°47'	—
101:101	10	61 49 —62 21	62 7	—
101:001	11	49 20 —50 35	50 4	50 6'
001:011	26	49 10 —49 33	49 27	—
011:010	7	40 21 —40 43	40 31	40 33
001:010	10	89 45 —90 15	90 0	90 0
101:011	15	75 28 —76 5	75 44	75 46
011:101	16	103 50 —104 39	104 17	104 14
101:011	12	65 8 —65 30	65 20	65 21
011:101	12	114 20 —114 52	114 41	114 39

## 24. 1:4-Chlorobromobenzene 2-sulpho-m-toluidide.

This compound crystallises readily from acetone in six-sided rhombs (m. p. 159.5°) the edges and corners of which are truncated. The four faces of the form {011} were useless for measurement, as they gave multiple reflexions in every case.

System: Monosymmetric.

Axial Ratios:  $a:b:c=0.7576:1:1.154$ ;  $\beta=100^{\circ}37'$ .

Equivalence Parameters:  $x:y:z=8.430:2.782:3.210$ . [4a.]

Forms observed: {011}, {10 $\bar{1}$ }, {110}, {101}, {001}.

Angle.	No of observations.	Limits.	Mean.	Calculated.
001:101	20	49° 0'—49° 58'	49° 27'	49° 28'
101:10 $\bar{1}$	47	65 52—66 31	66 12	—
10 $\bar{1}$ :00 $\bar{1}$	22	63 49—64 46	64 21	64 21
101:110	27	45 41—46 17	45 58	—
110:01 $\bar{1}$	7	69 20—69 40	69 30	69 30
01 $\bar{1}$ :10 $\bar{1}$	19	64 70—64 50	64 26	64 32
10 $\bar{1}$ :011	40	72 51—73 59	73 19	73 21
011:110	16	56 25—57 23	56 50	56 56
110:10 $\bar{1}$	28	49 12—50 13	49 43	—
110:110	6	73 7—73 42	73 21	73 21
110:110	6	106 25—106 57	106 36	106 39

## 25. 1:4-Chlorobromobenzene 2-sulpho-p-toluidide.

This toluidide crystallises readily from acetone in prisms (m. p. 157°) remarkable on account of the number of faces that in most cases are developed upon them. They show a decided resemblance in habit and dimensions to the stable form of the anilide.

System: Monosymmetric.

Axial Ratios:  $a:b:c=0.767:1:0.959$ ;  $\beta=96^{\circ}25'$ .

Equivalence Parameters: 9.022:2.940:2.820. [4a.]

Forms observed: {100}, {010}, {001}, {011}, {012}, {212}, {121}, {111}, {101}, {101}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100:101	4	41° 39'—42° 9'	41° 56'	41° 52'
101:001	11	56 14—56 53	56 33	—
100:001	5	98 16—98 41	98 30	98 25
111:111	31	57 24—58 42	58 3	58 1
111:121	24	18 8—19 57	18 55	18 57
011:012	23	25 1—25 45	25 23	25 23
012:011	21	17 30—18 36	18 5	18 7*
101:212	10	17 10—18 13	17 48	17 45
212:010	2	72 11—72 15	72 13	72 15
101:012	10	59 47—60 18	60 7	60 8
10 $\bar{1}$ :111	13	78 30—79 26	78 49	—
111:012	20	40 38—41 23	41 31	—
111:011	5	39 18—39 59	39 31	39 26

## 7. 1:4-Dibromobenzenesulphonic Chloride.

*p*-Dibromobenzenesulphonic chloride crystallises readily in measurable form from a mixture of benzene and light petroleum; it melts at  $71^{\circ}$ . (Found, Cl=10.79. Calc., Cl=10.61 per cent.)

System: Monosymmetric.

Axial Ratios:  $a:b:c=2.476:1:1.1439$ ;  $\beta=95^{\circ}26'$ .

Equivalence Parameters:  $x:y:z=5.787:2.337:2.674$ .

Forms observed:  $\{100\}$ ,  $\{111\}$ ,  $\{\bar{1}\bar{1}1\}$ ,  $\{100\}$ ,  $\{221\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100:111	19	$76^{\circ}2' - 76^{\circ}41'$	$76^{\circ}22'$	—
111: $\bar{1}\bar{1}1$	4	$33^{\circ}38' - 34^{\circ}30'$	$34^{\circ}1'$	$33^{\circ}51'$
$\bar{1}\bar{1}1:100$	4	$69^{\circ}41' - 69^{\circ}53'$	$69^{\circ}44'$	$69^{\circ}47'$
111: $\bar{1}\bar{1}\bar{1}$	11	$85^{\circ}39' - 86^{\circ}28'$	$85^{\circ}57'$	—
100:110	13	$67^{\circ}32' - 68^{\circ}15'$	$67^{\circ}55'$	—
110:110	7	$43^{\circ}33' - 44^{\circ}30'$	$44^{\circ}5'$	$44^{\circ}10'$
111:110	5	$39^{\circ}16' - 40^{\circ}42'$	$39^{\circ}51'$	$39^{\circ}55'$
110: $\bar{1}\bar{1}\bar{1}$	5	$38^{\circ}11' - 39^{\circ}31'$	$38^{\circ}37'$	$38^{\circ}28'$

## 8. 4:4-Dibromobenzenesulphonic Bromide.

*p*-Dibromobenzenesulphonic bromide crystallises well from a mixture of benzene and light petroleum in forms closely resembling the sulphonic chloride. It melts at  $114^{\circ}$ . [Found, (sulphonic) Br=20.96. Calc., Br=21.10 per cent.]

System: Monosymmetric.

Axial Ratios:  $a:b:c=2.479:1:1.1445$ ;  $\beta=96^{\circ}49'$ .

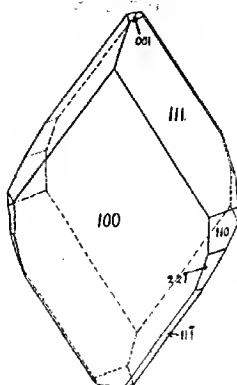
Equivalence Parameters:  $x:y:z=5.796:2.338:2.676$ .

Forms present:  $\{100\}$ ,  $\{111\}$ ,  $\{\bar{1}\bar{1}1\}$ ,  $\{110\}$ ,  $\{22\bar{1}\}$ ,  $\{001\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100:111	27	$77^{\circ}0' - 77^{\circ}29'$	$77^{\circ}12'$	—
111: $\bar{1}\bar{1}1$	6	$33^{\circ}41' - 34^{\circ}7'$	$33^{\circ}48'$	$33^{\circ}51'$
$\bar{1}\bar{1}1:100$	6	$68^{\circ}32' - 68^{\circ}49'$	$68^{\circ}41'$	$68^{\circ}57'$
111: $\bar{1}\bar{1}\bar{1}$	13	$85^{\circ}15' - 85^{\circ}40'$	$85^{\circ}29'$	—
100:110	18	$67^{\circ}25' - 68^{\circ}21'$	$67^{\circ}53'$	—
110:110	7	$44^{\circ}3' - 44^{\circ}27'$	$44^{\circ}14'$	$44^{\circ}14'$
$00\bar{1}:\bar{1}\bar{1}\bar{1}$	4	$49^{\circ}13' - 49^{\circ}18'$	$49^{\circ}15'$	$49^{\circ}18'$
111: $22\bar{1}$	6	$16^{\circ}8' - 16^{\circ}27'$	$16^{\circ}18'$	$16^{\circ}22'$
$22\bar{1}:110$	7	$21^{\circ}34' - 22^{\circ}2'$	$21^{\circ}45'$	$21^{\circ}48'$
110:111	11	$39^{\circ}53' - 40^{\circ}25'$	$40^{\circ}6'$	$40^{\circ}13'$
111:001	4	$52^{\circ}5' - 52^{\circ}27'$	$52^{\circ}18'$	$52^{\circ}19'$
100:001	8	$82^{\circ}40' - 83^{\circ}40'$	$83^{\circ}6'$	$83^{\circ}11'$
111: $\bar{1}\bar{1}0$	7	$53^{\circ}2' - 53^{\circ}42'$	$53^{\circ}18'$	$53^{\circ}21'$
$\bar{1}\bar{1}\bar{1}:111$	8	$78^{\circ}4' - 78^{\circ}41'$	$78^{\circ}22'$	$78^{\circ}23'$



Fig. 1.



p-Dibromobenzenesulphonic bromide.

## 19. 1:4-Dibromobenzenesulphanilide.

p-Dibromobenzenesulphanilide.—This substance was obtained in two forms, a labile and a stable form, under conditions exactly similar to those which gave rise to two forms of the chlorobromo-compound. In this case both forms were measured.

The *labile* form crystallises well from a solution of the pure substance in acetone; it melts at 143°.

System: Monosymmetric.

Axial Ratios:  $a:b:c = 1.392:1:1.163$ ;  $\beta = 97^\circ 56'$ .

Equivalence Parameters:  $x:y:z = 7.631:2.781:3.210$ . [2a.]

Forms present: {100}, {010}, {111},  $\{\bar{1}\bar{1}\bar{1}\}$ , {121}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
010 : 111	11	46°27'—46°51'	46°37'	—
010 : 121	8	27°33'—28°2'	27°44'	27°54'
121 : 111	8	18°38'—18°58'	18°49'	18°44'
010 : $\bar{1}\bar{1}\bar{1}$	20	50°2'—50°57'	50°29'	—
100 : 111	11	57°47'—58°41'	58°7'	58°12'
111 : $\bar{1}\bar{1}\bar{1}$	11	69°26'—70°15'	69°51'	—
$\bar{1}\bar{1}\bar{1}$ : 100	9	51°38'—52°18'	51°59'	51°57'
100 : 010	4	89°43'—90°16'	89°59'	90°0'

The *stable* form separates in measurable crystals from a solution of the substance in acetone containing a trace of aniline. It melts at 143°.

System: Monosymmetric.

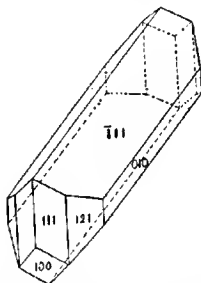
Axial Ratios:  $a:b:c = 1.329:1:1.025$ ;  $\beta = 97^\circ 58'$ .

Equivalence Parameters:  $x:y:z = 7.793:2.932:3.005$ . [2a.]

Forms present: {001}, {101},  $\{\bar{1}01\}$ , {111},  $\{\bar{1}\bar{1}\bar{1}\}$ , {121}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$10\bar{1} : 101$	11	$74^{\circ}47' - 75^{\circ}28'$	$75^{\circ} 7'$	—
$101 : 001$	14	$57 12 - 57 44$	$57 26$	$57^{\circ}26'$
$001 : 101$	12	$47 20 - 47 33$	$47 26$	$47 27$
$001 : 111$	14	$65 47 - 66 10$	$65 58$	—
$111 : 111$	8	$56 24 - 57 16$	$56 38$	$56 42$
$111 : 00\bar{1}$	6	$56 58 - 57 53$	$57 23$	$57 20$
$111 : 00\bar{1}$	15	$113 49 - 114 18$	$114 0$	$114^{\circ} 2$
$\bar{1}\bar{1}\bar{1} : 111$	8	$98 0 - 98 35$	$98 22$	$98 22$
$111 : 101$	19	$40 34 - 41 7$	$40 48$	$40 49$
$111 : 111$	16	$81 20 - 82 0$	$81 38$	—
$10\bar{1} : 111$	22	$36 24 - 37 42$	$37 5$	$37 3$
$111 : 121$	8	$18 58 - 19 51$	$19 22$	$19 25$
$121 : 121$	7	$67 2 - 67 8$	$67 6$	$67 4$
$111 : 121$	9	$49 1 - 49 34$	$49 17$	$49 17$
$12\bar{1} : 111$	9	$130 24 - 131 2$	$130 42$	$130 43$

FIG. 2.

Labile form of *p*-dibromobenzenesulphanilide.26. 1 : 4-Dibromobenzenesulpho-*p*-toluidide.

*p*-Dibromobenzenesulpho-*p*-toluidide separates readily in measurable forms from acetone. It melts at  $151^{\circ}$ .

System : Monosymmetric.

Axial Ratios :  $a : b : c = 0.7645 : 1 : 0.9595$ ;  $\beta = 98^{\circ}32'$ .

Equivalence Parameters :  $x : y : z = 9.001 : 2.943 : 2.824$ . [4a.]

Forms present :  $\{010\}$ ,  $\{100\}$ ,  $\{001\}$ ,  $\{101\}$ ,  $\{\bar{1}01\}$ ,  $\{011\}$ ,  $\{012\}$ ,  $\{111\}$ ,  $\{\bar{1}\bar{1}\bar{1}\}$ ,  $\{212\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated
$\bar{1}\bar{1}\bar{1} : 010$	42	$60^{\circ}32' - 61^{\circ}30'$	$61^{\circ} 2'$	—
$011 : 010$	26	$46 5 - 47 12$	$46 28$	—
$011 : \bar{1}\bar{1}\bar{1}$	28	$39 0 - 39 51$	$39 30$	—
$\bar{1}\bar{1}\bar{1} : 111$	37	$57 0 - 58 37$	$58 0$	$57^{\circ}56'$
$001 : 012$	19	$25 10 - 25 55$	$25 28$	$25 25$
$012 : 011$	24	$17 24 - 18 40$	$17 57$	$18 7$
$001 : 010$	9	$89 41 - 90 11$	$89 59$	$90 0$
$100 : 111$	3	$50 57 - 51 6$	$51 1$	$51 5$
$111 : 011$	5	$45 3 - 45 18$	$45 13$	$45 6$
$\bar{1}\bar{1}\bar{1} : 100$	6	$44 2 - 44 38$	$44 17$	$44 19$
$101 : 211$	6	$17 14 - 18 9$	$17 44$	$17 44$
$212 : 111$	5	$14 37 - 15 5$	$14 47$	$14 52$
$111 : 010$	3	$57 21 - 57 41$	$57 29$	$57 24$

27. *Methylic p-Dibromobenzenesulphonate.*

This crystallises readily from acetone. It melts at 63°.

System: Monosymmetric.

Axial Ratios:  $a : b : c = 1.167 : 1 : 2.443$ ;  $\beta = 94^{\circ}0'$ .

Equivalence Parameters:  $x : y : z = 2.930 : 2.454 : 5.995$ .

Forms present:  $\{100\}$ ,  $\{101\}$ ,  $\{\bar{1}01\}$ ,  $\{111\}$ ,  $\{210\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 210	23	49°59' — 51°26'	50°37'	—
210 : 210	9	78 17 — 79 17	78 39	78°46'
100 : 111	15	74 37 — 75 38	75 5	—
111 : $\bar{1}00$	15	104 36 — 105 27	104 57	104 55
101 : 111	10	46 26 — 47 54	47 13	—
111 : $\bar{1}11$	6	35 3 — 35 42	35 32	35 34
100 : 101	5	67 9 — 68 18	67 57	67 44
101 : $\bar{1}01$	6	50 19 — 51 38	51 2	51 3
$\bar{1}01$ : $\bar{1}00$	12	60 25 — 61 20	60 52	61 13
$\bar{1}01$ : 111	4	64 3 — 65 4	64 41	64 43
111 : 210	6	42 50 — 43 29	43 7	43 4
210 : $\bar{1}01$	5	71 34 — 72 53	72 16	72 13

28. *Ethylic p-dibromobenzenesulphonate.*

This separates fairly readily from acetone but the forms appearing are so few that very few angles have been measured. It melts at 106°.

System: Orthorhombic.

Axial Ratios:  $a : b : c = 1.124 : 1 : 0.9393$ .

Equivalence Parameters:  $x : y : z = 6.455 : 2.872 : 2.697$ . [2a.]

Forms observed:  $\{100\}$ ,  $\{101\}$ ,  $\{110\}$ ,  $\{010\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
010 : 110	11	41° 8' — 42° 4'	41°41'	—
010 : 011	34	46 29 — 47 21	46 49	—

9. *1:4-Iodochlorobenzene-2-sulphonic Chloride.*

*p-Iodochlorobenzenesulphonic chloride* is readily obtained in good prismatic crystals (m. p. 69°) from a mixture of benzene and light petroleum. [Found, (sulphonic) Cl = 10.53. Calc., Cl = 10.52 per cent.]

System: Monosymmetric.

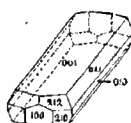
Axial Ratios:  $a : b : c = 0.729 : 1 : 0.654$ ;  $\beta = 99^{\circ}42'$ .

Equivalence Parameters:  $x : y : z = 3.095 : 4.247 : 2.778$ .

Forms present:  $\{010\}$ ,  $\{001\}$ ,  $\{021\}$ ,  $\{100\}$ ,  $\{210\}$ ,  $\{221\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 210	9	17°39'—18°11'	17°51'	17°52'
210 : 010	12	71 43—72 27	72 8	—
010 : 021	15	34 31—35 30	34 49	34 50
021 : 001	11	54 54—55 32	55 10	—
100 : 001	3	99 39—99 43	99 41	99 42
001 : 210	8	98 50—99 27	99 13	—
001 : 212	10	54 33—55 25	54 54	54 53
212 : 210	6	43 55—44 35	44 12	44 20
010 : 212	12	75 6—75 23	75 18	75 16
212 : 212	3	29 20—29 31	29 24	29 28
100 : 010	6	89 50—90 17	90 1	90 0
010 : 001	12	89 47—90 12	89 59	90 0

Fig. 3.



5-Chloro-2-iodobenzene-sulphonic chloride.

## v. 1:4-Iodochlorobenzene-2-sulphonic Bromide.

*Iodochlorobenzene-sulphonic bromide* crystallises readily from a mixture of benzene and light petroleum in four-sided prisms with pyramidal ends. Although differing entirely from *p*-dibromobenzene-sulphonic bromide in habit, when the correct faces are chosen as pinacoids the axial ratios deduced for this bromide are almost identical with those of that substance. It melts at 102°. [Found Br=21.30. Calc., Br=20.98 per cent.]

System: Monosymmetric.

Axial Ratios:  $a:b:c=2.469:1:1.154$ ;  $\beta=95^\circ 50'$ .

Equivalence Parameters:  $x:y:z=5.761:2.333:2.692$ .

Forms present: {100}, {101}, {111}, {210}.

Angle.	No of observations.	Limits.	Mean.	Calculated.
100 : 210	33	50°30'—51° 9'	50°51'	—
210 : 210	14	78 8—78 29	78 19	78°18'
101 : 111	19	47 6—47 32	47 17	—
111 : 111	5	85 13—85 34	85 25	85 26
100 : 101	12	69 29—70 12	69 48	—
210 : 111	4	43 59—44 11	44 5	44 9
100 : 111	2	76 14—76 21	76 18	76 27
101 : 210	10	77 6—77 37	77 24	77 26
210 : 111	3	65 1—65 13	65 5	65 3

## 20. 1:4-Iodochlorobenzene-2-sulphanilide.

This separates readily from acetone in a form closely resembling the stable forms of the anilides previously measured. It melts at  $168^{\circ}$ .

System: Monosymmetric.

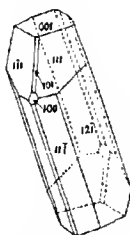
Axial Ratios:  $a:b:c=1.350:1:0.9971$ ;  $\beta=97^{\circ}15'$ .

Equivalence Parameters:  $x:y:z=7.943:2.942:2.933$ . [2a.]

Forms present:  $\{100\}$ ,  $\{001\}$ ,  $\{101\}$ ,  $\{10\bar{1}\}$ ,  $\{11\bar{1}\}$ ,  $\{111\}$ ,  $\{12\bar{1}\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$10\bar{1}:100$	7	$33^{\circ}35' - 33^{\circ}55'$	$33^{\circ}49'$	$33^{\circ}50'$
$100:101$	4	$38\ 51 - 39\ 4$	$38\ 58$	$38\ 56$
$101:001$	6	$58\ 4 - 58\ 25$	$58\ 14$	$58\ 19$
$100:001$	13	$97\ 1 - 97\ 29$	$97\ 15$	—
$001:101$	9	$48\ 32 - 49\ 7$	$48\ 50$	$48\ 55$
$001:111$	23	$66\ 5 - 66\ 49$	$66\ 23$	—
$111:11\bar{1}$	21	$55\ 2 - 55\ 42$	$55\ 22$	$55\ 19$
$11\bar{1}:00\bar{1}$	22	$57\ 57 - 58\ 34$	$58\ 15$	$58\ 18$
$11\bar{1}:111$	9	$99\ 14 - 99\ 37$	$99\ 24$	$99\ 24$
$111:101$	7	$40\ 13 - 40\ 23$	$40\ 16$	$40\ 18$
$111:11\bar{1}$	11	$80\ 23 - 80\ 56$	$80\ 36$	$80\ 36$
$10\bar{1}:11\bar{1}$	7	$36\ 46 - 37\ 31$	$36\ 56$	$36\ 56$
$11\bar{1}:121$	20	$19\ 0 - 19\ 52$	$19\ 21$	$19\ 26$
$12\bar{1}:121$	13	$67\ 15 - 67\ 31$	$67\ 23$	$67\ 16$
$100:111$	19	$53\ 26 - 53\ 48$	$53\ 37$	—
$111:111$	20	$77\ 39 - 78\ 18$	$77\ 57$	$77\ 59$
$111:100$	19	$48\ 7 - 48\ 44$	$48\ 25$	$48\ 24$
$111:121$	7	$48\ 4 - 48\ 46$	$48\ 25$	$48\ 25$
$111:12\bar{1}$	4	$65\ 29 - 65\ 45$	$65\ 35$	$65\ 35$

FIG. 4.



5-Chloro-2-iodobenzene-sulphanilide.

## 29. Ethylic 1:4-Iodochlorobenzene-2-sulphonate.

This separates from ether in thin, hexagonal plates melting at  $87^{\circ}$ .

System: Orthorhombic.

Axial Ratios:  $a:b:c=2.322:1:0.898$ .

Equivalence Parameters:  $x:y:z=6.697:2.883:2.589$ . [2a.]

Forms present:  $\{001\}$ ,  $\{100\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{201\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 110	21	66°10'—67°10'	66°42'	—
110 : 010	8	23 3 — 23 34	23 13	23°18'
110 : 110	7	46 9 — 47 6	46 35	46 36
100 : 010	10	89 47 — 90 20	89 59	90 0
100 : 111	17	73 22 — 74 27	73 57	—
111 : 111	6	31 51 — 32 13	32 4	32 6
100 : 201	12	51 45 — 52 53	52 9	52 18

## 14. 1 : 4-Iodobromobenzene-2-sulphonic Chloride.

From benzene and light petroleum this separates in forms that are very similar indeed to those of the corresponding chloriodo-compound. It melts at 97°. (Found, Cl = 9.32. Calc., Cl = 9.30 per cent.)

System : Monosymmetric.

Axial Ratios :  $a : b : c = 0.815 : 1 : 0.673$ ;  $\beta = 95^\circ 28'$ .

Equivalence Parameters :  $x : y : z = 3.291 : 4.040 : 2.719$ .

Forms present : {010}, {001}, {021}, {212}, {211}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
001 : 021	21	58°11'—58°35'	58°20'	—
021 : 010	17	31 17 — 31 54	31 39	31°40'
001 : 010	20	89 45 — 90 15	90 0	90 0
001 : 212	23	54 53 — 55 20	55 9	—
212 : 001	20	124 40 — 124 58	124 50	124 51
010 : 212	19	74 37 — 75 8	74 48	—
212 : 212	13	30 7 — 30 41	30 21	30 24
021 : 212	4	58 26 — 58 33	58 29	58 28
212 : 211	3	17 59 — 18 10	18 4	18 1

## 21. 1 : 4-Iodobromobenzene-2-sulphanilide.

This anilide separates readily from acetone. It melts at 150°.

System : Monosymmetric.

Axial Ratios :  $a : b : c = 1.329 : 1 : 0.979$ ;  $\beta = 97^\circ 18'$ .

Equivalence Parameters :  $x : y : z = 7.909 : 2.976 : 3.913$ . [2a.]

Forms present : {100}, {001}, {101}, {101}, {111}, {111}, {121}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 001	3	97° 4'—97°10'	97° 7'	97°18'
100 : 101	3	38 41 — 39 20	38 54	38 53
101 : 001	3	58 9 — 58 29	58 20	58 25
001 : 101	5	48 47 — 49 16	49 1	48 57
101 : 100	1	33°44'	33 44	33 45
111 : 111	20	79 14 — 80 5	79 40	—
111 : 111	20	99 56 — 100 43	100 19	100 20
101 : 111	7	36 15 — 36 55	36 33	36 27
111 : 121	6	18 55 — 19 23	19 7	19 27
121 : 121	15	68 3 — 68 27	68 12	—
001 : 111	35	65 40 — 66 48	66 17	—
111 : 111	17	55 11 — 56 8	55 28	55 36
111 : 001	19	57 49 — 58 35	58 22	58 7

As is generally the case, the face  $\{111\}$  is very badly represented, accounting for the discrepancy between the mean observed and calculated values of the angles over this face.

#### 10. 1:4-Chloriodobenzene-2-sulphonic Chloride.

This crystallises readily from a mixture of benzene and light petroleum. It melts at  $88^\circ$ . [Found, (sulphonic) Cl = 10.50. Calc., Cl = 10.52 per cent.]

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.583:1:1.176$ ;  $\beta = 99^\circ 7'$ .

Equivalence Parameters:  $x:y:z = 5.914:2.289:2.692$ .

Forms present:  $\{100\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{221\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 111	43	$78^\circ 47' - 79^\circ 21'$	$79^\circ 0'$	—
111 : 111	14	$32^\circ 42' - 33^\circ 14'$	$32^\circ 59'$	$32^\circ 57'$
111 : 100	14	$67^\circ 49' - 68^\circ 17'$	$68^\circ 3'$	—
111 : $\bar{1}\bar{1}\bar{1}$	18	$82^\circ 58' - 83^\circ 30'$	$83^\circ 18'$	—
$\bar{1}\bar{1}\bar{1}$ : $\bar{1}\bar{1}\bar{1}$	20	$96^\circ 35' - 97^\circ 8'$	$96^\circ 47'$	$96^\circ 47'$
111 : 221	6	$15^\circ 58' - 16^\circ 10'$	$16^\circ 3'$	$16^\circ 3'$
221 : 110	7	$21^\circ 12' - 21^\circ 33'$	$21^\circ 21'$	$21^\circ 22'$
110 : 111	8	$39^\circ 42' - 40^\circ 14'$	$39^\circ 58'$	$40^\circ 1'$
111 : $\bar{1}\bar{1}\bar{1}$	7	$102^\circ 20' - 102^\circ 46'$	$102^\circ 34'$	$102^\circ 34'$
100 : 110	8	$68^\circ 16' - 68^\circ 38'$	$68^\circ 25'$	$68^\circ 35'$

#### 12. 1:4-Bromiodobenzene-2-sulphonic Chloride.

This crystallises in a labile form from a mixture of benzene and light petroleum. It melts at  $91^\circ$ . (Found, Cl = 9.32. Calc., Cl = 9.30 per cent.)

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.555:1:1.158$ ;  $\beta = 94^\circ 23'$ .

Equivalence Parameters:  $x:y:z = 5.882:2.302:2.666$ .

Forms present:  $\{100\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{\bar{1}\bar{1}\bar{1}\}$ .

Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 111	10	$75^\circ 40' - 76^\circ 21'$	$76^\circ 8'$	—
111 : $\bar{1}\bar{1}\bar{1}$	10	$32^\circ 51' - 33^\circ 7'$	$33^\circ 1'$	—
111 : 100	8	$70^\circ 29' - 71^\circ 29'$	$70^\circ 51'$	$70^\circ 51'$
111 : $\bar{1}\bar{1}\bar{1}$	4	$94^\circ 27' - 94^\circ 44'$	$94^\circ 35'$	—
100 : 110	10	$68^\circ 32' - 68^\circ 54'$	$68^\circ 40'$	$68^\circ 34'$
111 : $\bar{1}\bar{1}\bar{1}$	5	$102^\circ 3' - 102^\circ 28'$	$102^\circ 13'$	$102^\circ 12'$
$\bar{1}\bar{1}\bar{1}$ : 110	3	$38^\circ 13' - 38^\circ 23'$	$38^\circ 18'$	$38^\circ 18'$

#### 22. 1:4-Chloriodobenzene-2-sulphonic Bromide.

This crystallises readily from benzene. It melts at  $143^\circ$ . (Found, Br = 21.10. Calc., Br = 20.98 per cent.)

System: Monosymmetric.

Axial Ratios:  $a:b:c = 2.567:1:1.167$ ;  $\beta = 100^\circ 30'$ .

Equivalence Parameters:  $x:y:z = 5.912:2.303:2.689$ .

Forms present:  $\{100\}$ ,  $\{001\}$ ,  $\{110\}$ ,  $\{111\}$ ,  $\{\bar{1}\bar{1}\bar{1}\}$ ,  $\{221\}$ .

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Angle.	No. of observations.	Limits.	Mean.	Calculated.
100 : 111	17	79° 38' — 79° 55'	79° 47'	—
111 : 100	19	100 1 — 100 30	100 14	100° 13'
100 : 110	14	68 12 — 68 33	68 23	—
110 : 110	6	43 8 — 43 27	43 14	43 14
111 : 111	10	96 23 — 97 26	96 44	96 44
111 : 111	10	82 45 — 83 39	83 17	83 16
100 : 001	5	100 9 — 100 45	100 29	100 30
001 : 100	5	79 10 — 79 47	79 30	79 30
001 : 111	7	53 5 — 53 38	53 22	53 20
111 : 110	11	40 17 — 40 45	40 31	—
110 : 221	17	21 15 — 21 40	21 23	21 28
221 : 001	8	64 28 — 64 53	64 45	64 41
100 : 221	8	66 8 — 66 34	66 20	66 24

## 16. 1 : 4-Dichlorobenzene-2-sulphonamide.

This substance crystallises from a mixture of acetone and ethylic acetate in bright plates, which are very much given to twinning. It melts at 182°.

System : Monosymmetric ;  $a : b : c = 0.423 : 1 : 0.421$  ;  $\beta = 91^{\circ}44'$ .

Equivalence Parameters : 2.573 : 6.079 : 2.558.

Forms present : {010}, {110}, {021}, {111}, {111}.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
010 : 110	19	66° 52' — 67° 16'	67° 4'	—
110 : 110	8	45 36 — 46 4	45 50	45° 52'
010 : 021	17	49 37 — 50 18	49 56	—
110 : 021	10	76 26 — 76 56	76 43	76 44
021 : 111	4	44 37 — 44 55	44 44	44 47
111 : 110	4	58 21 — 58 51	58 32	58 29
021 : 110	15	73 51 — 74 34	74 13	—
110 : 111	4	59 46 — 60 3	59 53	60 4
111 : 021	5	45 21 — 46 1	45 41	45 43
010 : 111	6	73 34 — 73 44	73 40	73 37

The substance exhibits pseudo-cubic symmetry, the parameters  $a$  and  $c$  being practically equal. This is evidence of the existence in the structure of the rhombohedral type of marshalling.

## CXLIX.—The Molecular Complexity of Amides in Various Solvents. Part II.

By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and WILLIAM ERNEST STEPHEN TURNER.

Two years ago the authors communicated the results of a study of the molecular complexity of eleven amides (simple and substituted) in each of the solvents, water, alcohol, acetone, chloroform, ether, and benzene (Trans., 1908, 93, 876). These solvents were suitable for our purpose by reason of their dielectric constants, which range, at ordinary temperatures, from about 80 in the case of



water to 2 for benzene. Our principal object was to test the soundness of what may be called the Nernst-Thomson rule, that the tendency of the solute to molecular association is hindered or allowed according as the dielectric constant of the solvent is high or low. We were successful to a considerable degree in demonstrating that the rule is sound. Special attention should be drawn to our results in the case of ether, which had been regarded as preventing association of the solute (Beckmann, *Zeitsch. physikal. Chem.*, 1890, 6, 455). We found that this solvent is an associating one, as by reason of its low dielectric constant it ought to be. In the case of water, however, we found important exceptions to the rule. We desired to confirm and extend these observations, particularly as regards ether and water. Other points of interest arose: for example, we wished to observe the alteration in the degree of association in the passage from member to member of a series of aliphatic amides.

In the investigation which we now describe, we examined seventeen additional substances of the amide type, including carhamides, anilides, and urethanes, using the same organic solvents as before. The data regarding amides in aqueous solution, which present some remarkable features, are reserved for another communication. The particular boiling-point process by which the molecular weights were determined has been subjected by one of us to a thorough scrutiny (Turner, this vol., p. 1184).

In our earlier paper we pointed out that the two methods of determining the amount of the solvent, by weighing, and by reading the volume of the solution—the method adopted by Lumsden and Walker—lead to results which differ little unless the solution is a concentrated one. We therefore adopted the volume method, with the proviso that we should make a special comparison of the extent of association of different substances only in dilute solution.

At the outset of the second part of our work, especially in view of the advance in accuracy obtained by using the new form of apparatus, we had to consider again how the amount of solvent should be determined.

It may be remarked that the difference between the two sets of molecular-weight data is to be ascribed chiefly to the inclusion, in the volume of the solution, of the solution-volume of the solute itself. The difference therefore should be least in those solutions in which contraction occurs when solvent and solute are mixed.

An endeavour has been made, when the solubility of the amides would allow of it, to determine the molecular weights of the various substances in solutions of approximately equimolecular concentration. As a consequence, the quantity of substance required is

greater the higher its molecular weight. At the same time, the greater proportion of the volume of the solution occupied by the solute results in a greater difference between the two sets of data (the weight and volume sets). On the whole, however, the actual percentage difference between the two sets, at the standard concentration adopted of 30 milligram-molecules per 100 c.c., is nearly the same, amounting to about 3 per cent.

In view of the smallness of the differences at the standard concentration, it appeared to us advantageous to adhere to the volume method, and thus to put ourselves in the position of being able to compare our present with our previous results. In order to illustrate the nature of the differences between the two methods, we have quoted both weight and volume results, for solutions in alcohol, acetone, benzene, and chloroform, of propionamide, as a typical aliphatic amide, and methylacetanilide, as containing the phenyl group. In the case of all other amides, in those solvents and in ether as well, we have given only the volume data.

#### EXPERIMENTAL.

Most of the materials were obtained from Kahlbaum, and were recrystallised until of constant melting point. The determination of this was carried out by means of a melting-point flask with long neck, and a series of standardised short-stem thermometers. The numbers enclosed in parentheses are those quoted by Beilstein: Propionamide 80° (79°), valeramide 126.5° (127°), *n*-butyramide 114–114.4° (115°), isobutyramide 127.5° (128–129°), isobutylacetamide 118–118.8° (120°), were crystallised from benzene; phenylcarbamide 146.5–147° (147°), diphenylcarbamide 239–240° (235°), phenylacetamide 157° (154–155°), urethane 49° (49–50°), from alcohol; ethylacetanilide 53° (54.5°), and methylacetanilide, of which the original specimen and all crops melted at 98–99° (101–102°), from ether; and lactanilide 58.5–59.1° (58°) from water. Formanilide, in the purification of which considerable difficulty was at first encountered, was finally found to yield beautiful, colourless, needle-shaped crystals when excess of the substance was boiled with light petroleum (b. p. 60–80°) and the excess allowed to solidify under the solvent, m. p. 47–47.5° (46°). The solvents were carefully purified and fractionally distilled as described in our previous communication. The constants used were as follows:

	Volume.	Weight.		Volume.	Weight.
Alcohol .....	1590	1170	Ether .....	3100	2160
Acetone .....	2270	1720	Benzene .....	3200	2610
Chloroform ..	2770	3900			

One change has been made in the constants used in the previous



## Solvent—Alcohol (continued).

V.	$\Delta$	N.	M.W.	V.	$\Delta$	N.	M.W.
Glycolanilide (M.W. 151), 1.805 grams.				Lactanilide (M.W. 165), 2.802 grams.			
26.1	0.749	48.0	164	26.3	0.865	53.1	161
33.3	0.600	37.8	161	33.8	0.853	41.2	186
41.0	0.500	30.8	147	44.7	0.520	31.2	153
50.5	0.411	24.3	145	54.7	0.413	25.5	162

## Urethane (M.W. 89.1), 1.799 grams.

V.	$\Delta$	N.	M.W.
22.6	1.391	89.4	91.1
29.7	1.049	68.1	91.9
35.2	0.876	57.3	92.7
42.7	0.720	47.2	92.9
49.7	0.615	40.6	93.8
57.3	0.527	35.3	94.6

## Phenylurethane (M.W. 165), 2.313 grams.

V.	$\Delta$	N.	M.W.
25.2	0.870	55.6	168
31.0	0.718	45.1	165
38.1	0.598	36.7	164
45.8	0.494	30.6	162
52.6	0.425	26.7	166

## Ethylacetyluride (M.W. 163), 2.327 grams.

V.	$\Delta$	N.	M.W.
25.2	0.934	58.6	157
32.5	0.719	43.9	158
40.4	0.587	35.3	156
50.0	0.474	23.5	156
60.0	0.400	23.8	154

## Phenylcarbamide (M.W. 136.1), 2.673 grams.

V.	$\Delta$	N.	M.W.
28.0	0.993	75.8	104
32.8	0.803	60.3	162
38.6	0.696	51.0	158
45.5	0.595	43.2	157
51.5	0.533	38.2	155

## Diphenylcarbamide (M.W. 212), 1.078 grams.

V.	$\Delta$	N.	M.W.
53.3	0.149	8.7	196
62.3	0.131	8.0	207

## Solvent—Acetone.

V.	$\Delta$	N.	M.W.	M.W.
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## Propionamide (M.W. 73.1), 1.238 grams.

V.	$\Delta$	N.	M.W.	M.W.
24.6	17.83	1.351	68.7	84.4
31.7	22.93	1.095	53.4	80.7
41.8	30.16	0.872	40.9	78.0
50.1	36.81	0.735	33.8	78.3

## Methylacetyluride (M.W. 149), 1.553 grams.

V.	$\Delta$	N.	M.W.	M.W.
22.8	16.17	1.076	45.6	143
29.8	21.42	0.829	34.9	143
35.4	25.78	0.692	29.4	144
43.8	31.63	0.571	23.8	141

## Acetanilide (M.W. 59), 1.015 grams.

V.	$\Delta$	N.	M.W.
23.1	1.361	74.3	72.9
29.6	1.136	53.1	68.6
37.7	0.927	45.6	66.0
45.3	0.742	35.6	64.3
55.2	0.667	31.2	62.6

## n-Butylamide (M.W. 87.1), 1.285 grams.

V.	$\Delta$	N.	M.W.
25.0	1.204	58.9	96.8
32.0	0.968	46.1	94.2
41.3	0.767	35.7	92.1
52.3	0.612	28.2	91.2

## iso-Butylamide (M.W. 87.1), 1.289 grams.

V.	$\Delta$	N.	M.W.
21.1	1.337	70.3	103.9
26.3	1.182	56.4	94.2
36.0	0.883	41.1	92.1
43.2	0.740	34.3	91.5
50.9	0.645	29.1	89.6

## Valeramide (M.W. 101.1), 1.330 grams.

V.	$\Delta$	N.	M.W.
26.3	1.081	60.1	106.4
32.0	0.898	41.1	105.2
39.2	0.761	33.5	101.2
46.1	0.656	28.5	99.7

## Solvent—Acetone (continued)

	N.	M.W.	V.	$\Delta$	N.	M.W.
<i>iso</i> Butylacetamide (M.W. 115.1), 1.784 grams.						
23.3	1.390	66.5	125	37.5	0.351	18.3
29.5	1.129	52.5	121	46.7	0.307	18.5
33.4	0.880	40.3	120	54.5	0.269	11.5
45.2	0.767	34.3	117			73.1
<i>Lactamide</i> (M.W. 89.1), 1.234 grams.						
27.8	0.902	49.8	111.6	<i>Phenylacetamide</i> (M.W. 135), 1.809 grams.		
34.4	0.752	40.2	108.1	26.3	1.036	51.0
41.1	0.663	33.7	102.8	33.2	0.842	40.4
47.9	0.584	28.9	98.4	39.4	0.714	34.0
				46.6	0.616	28.8
<i>Formanilide</i> (M.W. 121), 1.364 grams.						
26.3	0.977	42.9	121	<i>Glycollanilide</i> (M.W. 151), 1.904 grams.		
33.3	0.767	33.8	121	27.5	1.013	45.7
40.8	0.839	27.6	119	34.9	0.751	36.1
48.0	0.550	23.5	117	41.1	0.637	30.6
				49.6	0.568	25.4
<i>Lactanilide</i> (M.W. 165), 2.120 grams.						
25.6	1.118	50.0	168	<i>Urethane</i> (M.W. 89.1), 1.367 grams.		
32.4	0.900	39.7	165	31.2	1.072	49.2
39.1	0.754	32.9	164	39.1	0.865	39.3
45.5	0.848	28.2	164	46.9	0.714	32.7
				57.9	0.560	28.5
<i>Phenylurethane</i> (M.W. 165), 1.905 grams.						
22.4	1.203	51.4	160	<i>Ethylacetanilide</i> (M.W. 163), 2.000 grams.		
29.9	0.930	38.5	155	29.8	0.942	41.1
37.7	0.731	30.6	157	39.1	0.706	31.4
47.1	0.595	24.5	154	48.8	0.589	25.1
				59.4	0.471	20.6
<i>Phenylcarbamide</i> (M.W. 136), 1.238 grams.						
22.3	0.777	42.4	168	<i>Diphenylcarbamide</i> (M.W. 212), 1.163 grams.		
28.0	0.655	33.8	160	41.0	0.294	13.4
34.0	0.583	27.8	152	54.8	0.234	10.0
43.7	0.454	21.7	147			208

## Solvent—Chloroform.

V.	W.	$\Delta$ .	N.	M.W.	M.W.
<i>Propionamide</i> (M.W. 73.1), 0.896 gram.					
19.4	28.6	1.159	63.2	110.4	113.3
26.0	35.1	0.949	47.1	109.5	104.8
32.7	44.2	0.767	37.5	99.0	103.0
40.8	55.2	0.622	30.0	87.7	101.7
48.0	65.7	0.540	25.5	95.7	98.5
<i>Methylacetanilide</i> (M.W. 149), 0.9245 gram.					
22.2	30.5	0.816	28.0	142	145
28.9	38.7	0.657	21.5	135	142
38.0	51.4	0.491	16.3	137	143
47.6	65.2	0.382	13.0	141	145

*Solvent—Chloroform (continued).*

<i>V.</i>	$\Delta$ .	<i>N.</i>	<i>M.W.</i>	<i>V.</i>	$\Delta$ .	<i>N.</i>	<i>M.W.</i>
<i>Butyramide</i> (M.W. 87), 1.796 grams.				<i>isoButyramide</i> (M.W. 87), 1.646 grams.			
34.6	1.245	59.6	115.6	36.0	1.095	52.6	115.6
39.0	1.120	52.9	114.0	41.5	0.985	45.6	111.6
43.2	1.045	47.8	110.2	47.8	0.870	39.6	109.4
47.7	0.950	43.3	110.1	52.9	0.795	35.8	108.8
52.6	0.845	39.2	111.8	58.2	0.735	32.5	106.8

<i>Valeramide</i> (M.W. 101), 2.115 grams.				<i>isoButylacetamide</i> (M.W. 115), 1.715 grams.			
39.0	1.065	53.7	141	47.0	0.645	31.8	157
45.7	0.940	45.8	136	52.9	0.590	28.2	152
52.0	0.825	40.3	137	58.5	0.555	25.5	146
58.3	0.750	35.9	134	64.2	0.490	23.2	151
64.9	0.685	32.3	132				

*Phenylacetamide* (M.W. 135), 1.653 grams.

39.7	0.695	31.0	167
46.3	0.645	26.6	154
52.4	0.550	23.5	160
60.6	0.475	20.3	160

*Formanilide* (M.W. 121), 1.430 grams.

22.2	1.050	53.2	170
29.2	0.847	40.5	160
35.8	0.680	33.0	163
42.6	0.599	27.7	155

*Glycollanilide* (M.W. 151), 2.026 grams.

37.5	0.490	35.8	305
44.0	0.480	30.5	266
50.8	0.440	26.4	251
57.3	0.405	23.4	242

*Lactanilide* (M.W. 165), 2.125 grams.

45.5	0.535	28.3	242
51.6	0.485	25.0	235
57.7	0.450	22.3	227
62.7	0.430	20.5	218
68.8	0.415	18.7	206

*Urethane* (M.W. 89), 1.617 grams.

33.6	1.185	54.1	111.6
39.4	1.030	46.1	110.4
46.3	0.905	39.2	106.9
52.7	0.790	34.4	107.5
58.8	0.685	31.2	112.1

*Phenylurethane* (M.W. 185), 2.234 grams.

42.4	0.870	32.7	171.5
48.6	0.745	28.5	175
55.4	0.645	25.0	177
60.0	0.590	23.1	179
65.2	0.555	21.2	175

*Ethylacetanilide* (M.W. 163), 2.218 grams.

51.5	0.805	26.4	118
56.9	0.765	23.9	141
62.7	0.715	21.7	137
67.8	0.645	20.1	140.5

*Solvent—Ether.*

<i>V.</i>	$\Delta$ .	<i>N.</i>	<i>M.W.</i>	<i>V.</i>	$\Delta$ .	<i>N.</i>	<i>M.W.</i>
<i>Propionamide</i> (M.W. 73.1), 0.3610 gram.				<i>Methylacetanilide</i> (M.W. 149), 1.532 grams.			
38.3	0.325	12.9	89.9	34.7	0.880	29.6	155.5
39.8	0.315	12.4	89.3	47.9	0.645	21.5	154
41.8	0.325	11.8	82.4	49.4	0.630	20.8	153
43.8	0.330	11.3	77.4	50.5	0.620	20.4	152

## Solvent—Ether (continued)

$\Delta$	$N_r$	M.W.	$V$	$\Delta$	$N_r$	M.W.	
isoButylacetamide (M.W. 115), 0.540 gram.			Formanilide (M.W. 121), 1.052 grams.				
40.5	0.285	11.8	156	39.1	0.575	22.2	145
42.4	0.260	11.1	152	41.4	0.550	21.0	143
44.5	0.250	10.5	150.5	43.7	0.530	19.9	141
46.6	0.245	10.1	147	45.9	0.520	18.9	137
49.0	0.235	9.6	145	47.9	0.505	18.2	135
Glycollanilide (M.W. 151), 0.5348 gram.			Lactanilide (M.W. 165), 1.978 grams				
36.4	0.275	9.7	165	33.4	0.725	31.2	220
39.5	0.250	9.0	163	39.8	0.705	30.1	219
41.8	0.260	8.5	152	44.0	0.870	27.2	208
43.8	0.245	8.1	154	46.5	0.640	25.8	206
45.3	0.230	7.8	156	Phenylurethane (M.W. 166), 2.940 grams.			
Urethane (M.W. 89.1), 1.013 grams.			39.5	1.345	45.1	172	
37.2	0.810	30.6	104.2	42.9	1.260	41.5	169
39.4	0.785	28.8	104.2	51.4	1.040	84.7	170.5
42.0	0.740	27.1	101.0	62.0	0.860	28.7	171
44.0	0.710	25.8	100.5	Rhyllacetanilide (M.W. 163), 2.491 grams.			
36.4	1.225	42.0	173				
38.4	1.180	39.8	170.5				
48.6	0.960	32.8	173				
48.6	0.940	31.5	169				
Solvent—Benzene.							
$V$	$W$	$\Delta$	$N_r$	M.W.	M.W.		
Propionamide (M.W. 73.1), 0.942 gram.							
22.7	17.97	0.854	56.7	155	160		
33.4	26.89	0.687	38.5	131	133		
45.2	36.37	0.545	28.5	122	124		
60.2	48.39	0.446	21.4	112	114		
Methylacetanilide (M.W. 149), 1.803 gram.							
26.4	20.51	1.483	45.8	147	155		
39.2	30.81	0.987	30.8	149	155		
52.2	41.36	0.754	23.2	147	151		
$V$	$\Delta$	$N_r$	M.W.	$V$	$\Delta$	$N_r$	M.W.
n-Butyramide (M.W. 87.1), 1.288 grams.				isoButyramide (M.W. 87.1), 1.269 grams.			
29.2	0.844	50.7	168	29.2	0.842	49.8	165
42.7	0.647	34.6	149	42.3	0.665	34.4	144
57.5	0.523	25.8	137	57.9	0.549	25.2	128
1.054 grams.				0.951 gram.			
27.0	0.784	44.8	163	25.0	0.788	43.6	154
40.0	0.587	30.3	144	37.2	0.605	29.3	135
52.8	0.487	22.9	136	48.8	0.502	22.6	125

## Solvent—Benzene (continued).

V.	$\Delta$ .	N.	M.W.	V.	$\Delta$ .	N.	M.W.
Valeramide (M.W. 101.1), 1.432 grams.				isoButylacetamide (M.W. 115.1), 1.431 grams.			
26.6	0.941	53.2	183	28.1	0.851	44.2	191
53.4	0.741	36.3	161	40.7	0.670	30.5	168
51.2	0.602	27.6	149	53.7	0.558	23.1	153
64.0	0.504	22.1	142	65.3	0.475	19.0	143
Formanilide (M.W. 121), 1.435 grams.				Glycollanilide (M.W. 151), 1.132 grams.			
27.2	1.006	43.5	168	26.0	0.549	28.7	254
39.5	0.752	30.0	154	37.4	0.451	20.0	215
53.3	0.597	22.2	144	50.7	0.370	14.8	194
				64.2	0.304	11.7	185
Lactanilide (M.W. 165), 1.293 grams.				Urethane (M.W. 89.1), 1.450 grams.			
24.1	0.639	32.5	269	27.8	1.189	58.4	140
36.1	0.493	21.7	230	41.0	0.852	39.7	133
47.6	0.406	16.4	214	53.9	0.666	30.2	129
61.0	0.338	12.8	201				
Phenylurethane (M.W. 165), 2.140 grams.				Ethylacetanilide (M.W. 163), 2.021 grams.			
28.3	1.514	49.8	172	28.7	1.442	43.2	157
39.7	1.011	32.7	171	44.1	0.940	28.1	156
64.1	0.749	23.9	171	62.7	0.630	19.8	164

## Discussion of Results.

It is not always easy to draw a dividing line between the substances which do and those which do not form associated molecules. We have so far met the difficulty by assuming association to exist where the molecular-weight values exceed the normal by 10 per cent. at the concentration of 30 milligram-molecules per 100 c.c. Our observations were, of course, confined within the solubility limit of the amides, and this limitation is most serious in the case of solutions in ether.

## I.—The Influence of the Solvent in Hindering or Allowing Association of the Solute.

That a relation exists between the dielectric constant of the solvent and the degree of association of the solute can be seen from the following summary of the results. Those of the previous investigation are included, and are indicated by an asterisk. The dielectric constants ought to be those of the solvents at the boiling point, but we can only quote available data:



Solvent	Alcohol	Acetone	Chloroform	Ether	Benzene
No. of amides investigated ...	11*+17	10*+17	9*+15	4*+9	9*+12
" " which form simple molecules .....	24	20	3 and 1 doubtful	3 and 2 doubtful	3 and 1 doubtful
No. of amides which form associated molecules .....	1 and 3 doubtful	4 and 3 doubtful	18	9	17
Dielectric constant of solvent..	25.4 at 18.5°	21.2 at 22°	5 at 22°	4.4 at 18°	2.3 at 18°

We give the following notes in amplification of the above summary:

1. *Alcohol*: phenylcarbamide is associated, carbamide,\* malonamide,\* and propionamide\* are doubtful.

2. *Acetone*: acetamide,\* propionamide, lactamide, and phenylcarbamide are associated, butyramide, isobutyramide, and phenylacetamide are doubtful.

3. *Chloroform*: benzanilide,\* methylacetanilide, ethylacetanilide, and phenylurethane are unassociated.

4. *Ether*: methylacetanilide, phenylurethane, and ethylacetanilide are unassociated, salicylamide\* and glycollanilide are doubtful.

5. *Benzene*: methylacetanilide, ethylacetanilide, and phenylurethane are unassociated, benzanilide\* is doubtful.

The fact that alcohol and acetone cannot be regarded absolutely as non-associating solvents is in accordance with the relation which we find to hold between the dielectric constant and the degree of association of the solute. For we should expect a substance which is markedly associated in benzene with a dielectric constant of 2.3 to reveal its tendency to association, although only to a slight and ill-defined extent, in solvents like alcohol and acetone, the dielectric constants of which are 25 and 21 respectively.

As before, we have calculated the molecular weights and association factors at the concentration of 30 milligram-molecules per 100 c.c. in the solvents benzene, ether, and chloroform. The following table includes all our results, those of the previous paper being shown by an asterisk. The older chloroform data have been recalculated, using the new constant (p. 1607).

Propionamide, isobutylacetamide, and glycollanilide are not sufficiently soluble in ether to render possible even an estimate of the degree of association at the concentration of 30 milligram-molecules per 100 c.c. There can be no doubt that propionamide and isobutylacetamide are associated at the maximum concentration of about 12, and glycollanilide seems to be at 10. Special attention must be drawn to the three substances phenylurethane, methylacetanilide, and ethylacetanilide. They are unassociated in each of the five organic solvents, and might therefore be disregarded.

	Molecular weights in			Association factors in		
	Benzene.	Ether.	Chloroform.	Benzene.	Ether.	Chloroform.
Acetamide*	—	—	81.5	—	—	1.38
Monochloroacetamide*	130	—	121.5	1.39	—	1.30
Dichloroacetamide*	178	160	163	1.39	1.25	1.27
Trichloroacetamide*	210	187	217	1.29	1.15	1.27
Propionamide	124	—	98.3	1.70 (associated)	—	1.34
n-Butyramide	143	—	110	1.64	—	1.26
iso-Butyramide	136	—	106	1.56	—	1.22
Valeramide	152	—	130.5	1.53	—	1.29
iso-Butylacetamide	167	—	154	1.45 (associated)	—	1.33
Urethane	129	104	105	1.45	1.17	1.18
Phenylurethane	170	170.5	173	1.03	1.03	1.05
Trichloroacetamide*	294	—	—	1.52	—	—
Glycollanilide	258	—	265	1.70 (association doubtful)	—	1.75
Lactanilide	258	218	213	1.56	1.32	1.47
Formanilide	154.5	164	160	1.27	1.35	1.32
Acetanilide*	205	—	169.5	1.52	—	1.26
Methylacetanilide	149	156	146	1.00	1.04	0.98
Ethylacetanilide	156	171	154	0.96	1.05	0.94
Phenylacetamide	—	—	165	—	—	1.22
Benzamide*	184	—	152	1.52	—	1.26
Benzanilide*	228	—	218	1.17	—	1.10
Salicylanilide*	186	—	161	1.36	—	1.17

as having no tendency to association in organic solvents, and therefore as affording no test of the Nernst-Thomson rule. We have preferred to include them, so as to make an underestimate, rather than the opposite, of the extent of agreement with the rule. Even so, our results are sufficient to justify the rule in the case of organic solvents.

## II.—The Constitution of the Amide and the Extent of Association.

With the data we have now collected we are able to illustrate the influence of constitution on the tendency of the amide to form associated molecules. This tendency is shown to the greatest extent in benzene solution, and the data presented above, showing the degree of association at a certain concentration, allow of the following deductions:

(1) The molecules of the aliphatic amides are strongly associated, and (2), as is known to be the case in the homologous series of acids and alcohols, the extent of association decreases with increasing molecular weight. (3) The phenyl group depresses the tendency to association; thus, not only are the aromatic amides associated to a smaller extent than the aliphatic, but the anilide is less strongly associated than the corresponding amide, and phenylurethane much less than urethane. (4) The substitution of both hydrogen atoms of the amide, as in methyl- and ethyl-acetanilide, yields a substance of normal molecular size.

To consider the converse of the matter, we cannot think that

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determinations of molecular complexity can be questions of  
chemical constitution. No one maintains now that the hydroxyl  
group is the only cause of association, and that the amides  
which show a tendency to association have therefore the hydroxylic  
constitution. That hypothesis regarding the amides, as the sole  
explanation of the phenomena, was refuted first by Auwers (*Zeitsch.  
physikal. Chem.*, 1899, 30, 541, 542). But the suggestion which he  
made then, that the tervalent nitrogen atom may have as much  
to do with the association of amides as the hydroxyl group, is not  
confirmed by our observations regarding methyl- and ethyl-  
acetanilide. These substances show no tendency to association in  
organic solvents, whilst acetanilide is associated in benzene, chloro-  
form, and ether. These facts are sufficient to illustrate the difficulty  
of tracing all the complexities of this problem.

The materials used in this investigation were obtained by means  
of grants from the Government Grant Committee of the Royal  
Society and the Executive Committee of the Carnegie Trust for the  
Universities of Scotland.

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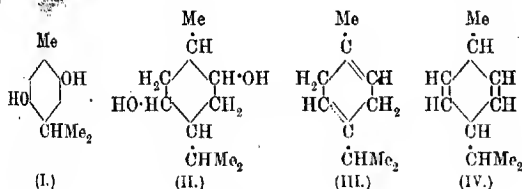
CL.—Contributions to the Chemistry of the Terpenes.  
Part VII. *Synthesis of a Monocyclic Terpene  
from Thymol.*

By GEORGE GERALD HENDERSON and MAGGIE MILLEN JEFFS  
SUTHERLAND, B.Sc. (Carnegie Research Scholar).

SEVERAL monohydric alcohols of the cyclohexane series have already  
been prepared by the hydrogenation of monohydric phenols in  
presence of nickel according to Sabatier and Senderens's method,  
but, so far as we are aware, the reaction has not hitherto been  
extended to any dihydric phenol. It appeared of interest to  
investigate the behaviour of a dihydric phenol of the formula  
 $C_{10}H_{12}(OH)_2$  when heated to the requisite temperature with  
hydrogen in the presence of finely divided nickel, in the hope that  
it would unite additively with hydrogen and yield a dihydroxy-  
menthane of the formula  $C_{10}H_{18}(OH)_2$ , and that from this glycol  
we could obtain a monocyclic terpene, one of the menthadienes, by

elimination of the elements of water. This expectation has been realised. Starting with thymol (3-hydroxycymene), we prepared 6-nitrosothymol (thymoquinoneoxime), reduced this to the corresponding amino-derivative, oxidised the latter to thymoquinone, and by reduction of the thymoquinone with sulphurous acid obtained thymoquinol,  $C_{10}H_{12}(OH)_2$ . This dihydric phenol was found to be susceptible of direct hydrogenation by the method of Sabatier and Senderens, and gave the desired product, *menthane-2:5-diol*,  $C_{10}H_{18}(OH)_2$ . Finally, when the glycol so prepared was heated with potassium hydrogen sulphate, it lost the elements of 2 molecules of water, and yielded an unsaturated hydrocarbon of the formula  $C_{10}H_{16}$ , which exhibited the properties of a monocyclic terpene.

Considering its relationship to thymoquinol (formula I), it is clear that the dihydroxymenthane must have the constitution represented in formula II. The terpene derived from the dihydroxymenthane should contain two ethylenic linkings in the ring, or, in other words, should be isomeric with  $\alpha$ -terpinene. Probably it is either  $\Delta^{1:4}$  (formula III) or  $\Delta^{2:5}$ -menthadiene (formula IV). The quantity of the terpene at our disposal did not permit of experiments being instituted to determine the relative positions of the double bonds, but we hope to be able to examine it more fully later.



#### EXPERIMENTAL.

*Preparation of Menthane-2:5-diol.*—6-Nitrosothymol was obtained by Klages' method (*Ber.*, 1899, **32**, 1518), which gave very satisfactory results. The 6-nitrosothymol was then converted into thymoquinone in the following manner. Twenty-five grams of the nitroso-compound were dissolved in 250 c.c. of 10 per cent. aqueous ammonia, and the solution was saturated with hydrogen sulphide. The precipitate of 6-aminothymol, which separated, was collected, washed with water, and dissolved in 450 c.c. of 3 per cent. sulphuric acid, and to the solution 500 c.c. of water and 250 c.c. of a 10 per cent. solution of potassium dichromate were added. After about half an hour the precipitate which had formed was collected, and dissolved in ten times its weight of glacial acetic acid. Chromic

anhydride was added to this solution in small quantities at a time until the oxidation was completed, and the thymoquinone was then precipitated by addition of water, collected, and dried. The yellow crystals of the quinone melted at 45°.

From the thymoquinone the corresponding quinol was prepared by reduction with sulphurous acid, as described by Carstanjen (*J. pr. Chem.*, 1871, [ii], 3, 50), and the following method was adopted for its hydrogenation. A long combustion tube, containing finely divided nickel, which was prepared by reducing the pure oxide, in a fine state of division, with hydrogen at as low a temperature as possible, was heated in an air-bath, a porcelain boat containing the substance was placed in the front part, and a fairly rapid current of hydrogen was passed through the tube. The hydrogen, of course, was carefully purified and dried. A number of preliminary experiments had shown that the most favourable temperature for the hydrogenation of the quinol was 190–200°, and accordingly the temperature of the tube was maintained at that point. Under these conditions an extremely viscous liquid slowly distilled from the tube, and was collected in a cooled receiver to which a U-tube filled with glass wool was attached. At first the distillate was quite colourless, but the last portion which passed over had a brown tinge. When the distillate was kept in the ice-chest, crystals began to form, but the process was very slow. The viscous liquid was therefore stirred with a small quantity of benzene, with the result that the greater part of it quickly became crystalline. The crystals were drained from a small proportion of an oily substance with which they were mixed, and recrystallised several times from benzene. The purified product was analysed, and found to be the desired dihydroxymenthane:

0.1262 gave 0.3210  $\text{CO}_2$  and 0.1322  $\text{H}_2\text{O}$ .  $\text{C} = 69.4$ ;  $\text{H} = 11.6$ .

0.1240 „ 0.3160  $\text{CO}_2$  „ 0.1310  $\text{H}_2\text{O}$ .  $\text{C} = 69.5$ ;  $\text{H} = 11.7$ .

$\text{C}_{10}\text{H}_{20}\text{O}_2$  requires  $\text{C} = 69.8$ ;  $\text{H} = 11.6$  per cent.

*Menthane-2:5-diol*,  $\text{C}_{10}\text{H}_{18}(\text{OH})_2$ , crystallises from benzene in very small, colourless plates, which melt at 112°. When dry, it has the form of a white powder, and it has no odour. It is very readily soluble in alcohol, ether, light petroleum, or hot benzene, and readily so in cold benzene. Hot water dissolves it sparingly, cold water scarcely at all. It distils without decomposition under diminished pressure (h. p. about 155°/15 mm.), or in a current of hydrogen at the ordinary pressure.

The small quantity of an oily substance which was separated from the crystalline menthane-2:5-diol during the process of purification was collected and fractionally distilled under diminished pressure in an atmosphere of dry carbon dioxide. Under 15 mm.

pressure a small fraction distilled at 80—100°, a still smaller fraction at 100—140°, and the bulk at 150—160°. The highest fraction solidified on cooling, and was found to consist almost wholly of menthane-2:5-diol. The fraction which distilled at 80—100° was too small in quantity to permit of satisfactory purification, but when treated with semicarbazide hydrochloride and potassium acetate in the usual manner it yielded a little of a crystalline solid. When purified by crystallisation from alcohol, in which it is very sparingly soluble, this compound forms small crystals, which are almost colourless, and melt and decompose at 243—244°. It is almost insoluble in water or ether. From an analysis, of which the result is quoted below, it appears not improbable that the compound is the disemicarbazono of a diketone of the formula  $C_{10}H_{16}O_2$  derived from the disecundary alcohol, menthane-2:5-diol:

0.1132 gave 29 c.c.  $N_2$  at 18° and 748 mm.  $N = 29.2$ .

$C_{12}H_{22}O_2N_6$  requires  $N = 29.6$  per cent.

*Preparation of a Menthadiene from Menthane-2:5-diol.*—An intimate mixture of menthane-2:5-diol with twice its weight of dry powdered potassium hydrogen sulphate was placed in a flask attached to a reflux condenser, and heated in a bath of fusible metal. When the temperature of the bath approached 190° a vigorous reaction began, and a colourless liquid vaporised and condensed in the tube. After having been heated for about half an hour at 190—200°, the mixture was cooled and distilled in a current of steam. A mobile, colourless liquid distilled with the steam and floated on the surface of the water in the receiver. The liquid was extracted with ether, the ethereal solution dried, the ether removed by distillation, and the residual liquid again mixed with potassium hydrogen sulphate and heated as before. The resulting mixture was distilled in a current of steam, the liquid extracted from the distillate with ether, the ethereal solution dried, and the ether distilled off. The liquid remaining in the flask was repeatedly distilled over sodium until no sign of any reaction could be observed, and finally we obtained a small quantity of a substance of practically constant boiling point, which analysis showed, to have the composition of a terpene:

0.1540 gave 0.4963  $CO_2$  and 0.1636  $H_2O$ .  $C = 87.9$ ;  $H = 11.8$ .

0.2897 „ 0.9358  $CO_2$  „ 0.3024  $H_2O$ .  $C = 88.1$ ;  $H = 11.6$ .

$C_{10}H_{16}$  requires  $C = 88.2$ ;  $H = 11.8$  per cent.

The terpene thus obtained is, as already stated, probably one of the isomeric terpinenes not hitherto described. It is colourless, has a rather faint odour somewhat like that of limonene, and a characteristic burning taste like oil of turpentine. Its boiling point is 179°/760 mm.;  $n_D^{20} = 1.4779$ ; the specific gravity is somewhat

greater than 0.84, but the quantity of the substance available was too small for an exact determination, especially as it appears to polymerise on keeping. It is practically insoluble in water, but dissolves in the usual organic solvents. It at once decolorises a dilute alkaline solution of potassium permanganate. When mixed with a solution of dry bromine in dry chloroform, it instantly unites with the bromine to form an additive compound, but the product must be unstable under the conditions of the experiment, since when rather more than three atomic proportions of bromine had been added, evolution of hydrogen bromide began. When treated with nitrous acid according to Wallach's method, the liquid turns yellow, but no crystalline nitrosite could be isolated. We hope to be able to complete the examination of this terpene before long.

It is our intention to endeavour to obtain terpenes from other monohydric phenols isomeric with thymol on the lines indicated in this paper.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

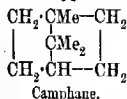
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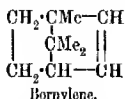
# CLI.—Contributions to the Chemistry of the Terpenes. Part VIII. Dihydrocamphene and Dihydro- bornylene.

By GEORGE GERALD HENDERSON and ERNEST FERGUSON POLLOCK.

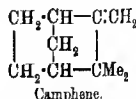
ACCORDING to the view now generally accepted as the most probable one, the arrangement of the carbon atoms in the molecule of bornylene is the same as in that of the saturated hydrocarbon camphane, whilst the structure of the molecule of camphene is of a different type, as is shown in the following formulae:



Camphane.

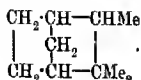


Bornylene.



Camphene.

If this conception of the molecular structure of these hydrocarbons be correct, it follows that dihydrobornylene,  $\text{C}_{10}\text{H}_{18}$ , should be identical with camphane, and that dihydrocamphene,  $\text{C}_{10}\text{H}_{18}$ , should have the constitution shown in the formula



We have recently carried out a number of experiments with the object of throwing light on this point, and have ascertained that, in accordance with theory, when bornylene is hydrogenated, camphane is produced, and that camphene yields a dihydro-compound which is certainly not camphane.

The preparation of *dihydrobornylene* has not hitherto been described, but we have found that it can be obtained easily from bornylene by the application of Sabatier and Senderens' method. The bornylene used in our experiments was prepared from borneol, through methyl bornyl xanthate, according to the very satisfactory process of Tschugaeff (*Ber.*, 1899, **32**, 3332); it melted at 103°, boiled at 149–150°, and was optically inactive. A porcelain boat containing bornylene was placed in the front part of a long tube containing finely divided nickel, which was prepared by reducing pure nickel oxide with hydrogen at the lowest possible temperature, and a current of carefully purified and dried hydrogen was passed at such a rate that from 2 to 3 grams of bornylene were carried through the tube in one hour. The tube was maintained by means of an air-bath at a temperature of 170–190°, which preliminary experiments had shown to be the most favourable one, and the solid dihydrobornylene which passed over was collected in a cooled receiver. Hydrogenation took place readily, and the product contained little or no unchanged bornylene; it was finally purified by crystallisation from methyl alcohol. The dihydrobornylene so prepared separates from methyl alcohol in small, white crystals, which have a faint odour somewhat like that of borneol. It melts at 150°, boils at 161–162° under the ordinary pressure, and sublimes easily, forming colourless, lustrous crystals. When treated with bromine and with potassium permanganate, it shows the character of a saturated hydrocarbon. In all these respects dihydrobornylene is exactly similar to camphane, and there can be no doubt as to their identity.

Dihydrocamphene has already been described by several observers, but their statements are somewhat contradictory. By heating isoborneol with zinc dust for a short time at 220°, Semmler (*Ber.*, 1900, **33**, 776) obtained a hydrocarbon,  $C_{10}H_{18}$ , which boiled at 162°, and separated from alcohol in fern-like aggregates of crystals, of which the melting point was 85°. This hydrocarbon was probably dihydrocamphene. Sabatier and Senderens (*Compt. rend.*, 1901, **132**, 1254) applied their method of hydrogenation in presence of nickel to camphene, and obtained a liquid hydrocarbon of the formula  $C_{10}H_{18}$ , which boiled at 164–165°. Finally, Vavon (*Compt. rend.*, 1909, **149**, 997) found that camphene in ethereal solution absorbs hydrogen when agitated with platinum black; and



yields a solid compound,  $C_{10}H_{18}$ , which is similar to camphene in appearance, but melts at  $87^{\circ}$ .

Using the same arrangement as in the case of bornylene, we examined the action of hydrogen on camphene in presence of heated nickel, and found in the first place that under these conditions camphene does not unite with hydrogen either so easily or so completely as bornylene. The camphene which we employed melted at  $54^{\circ}$ , and boiled at  $160^{\circ}$ . A number of observations were made at different temperatures, and in some cases the product was passed a second or even a third time through the heated tube. The results of numerous experiments may be summarised as follows. At temperatures ranging from  $120^{\circ}$  to  $180^{\circ}$  the product was a solid, resembling camphene in appearance, but melting at about  $64^{\circ}$ . At a temperature of  $200-220^{\circ}$ , the product was a mixture of a solid with a colourless liquid. At about  $240^{\circ}$  the product was a colourless, somewhat viscous liquid—in all probability the same substance as was obtained by Sabatier and Senderens. The solid product, melting at  $64^{\circ}$ , when tested with bromine gave evidence of the presence of a small proportion of an unsaturated hydrocarbon. It was subjected to repeated fractional crystallisation from methyl alcohol, and was ultimately proved to be a mixture of the dihydrocamphene described by Vavon with a little unchanged camphene. The liquid product formed at  $240^{\circ}$  was also found, by means of bromine, to contain a little of an unsaturated substance. When cooled in the ice-chest, it gradually solidified, and on subsequent exposure to the ordinary temperature part remained solid, while the other part became liquid again. The liquid part was poured off and again cooled, and then kept at the ordinary temperature, when a further yield of the solid was obtained. Finally, by frequent repetition of this procedure, almost the whole of the original liquid was obtained in solid form. The solid was ultimately separated by repeated fractional crystallisation from methyl alcohol into the dihydrocamphene of Vavon and a little unchanged camphene. It was thus shown that the liquid which we obtained by the hydrogenation of camphene according to Sabatier and Senderens' method is a mixture of dihydrocamphene with some unchanged camphene and a little of a third substance which was not further investigated. The dihydrocamphene obtained is saturated towards bromine or towards potassium permanganate, but it has a melting point widely different from that of camphene, is quite unlike it in appearance, and is undoubtedly a different substance.

We are indebted to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expense of this work.

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CLII.—*The Chlorination of Toluene.*

By JULIUS BEREND COHEN, HARRY MEDFORTH DAWSON,  
JOHN REGINALD BLOCKEY, and ARNOLD WOODMANSEY.

A PRELIMINARY note on the above subject was published in 1905 (*Trans.*, **87**, 1034), and in this an account was given of the action of chlorine obtained by the electrolysis of aqueous hydrochloric acid in contact with boiling toluene. The results pointed to a marked difference in the products so obtained from those which are produced by the action of ordinary chlorine under similar conditions.

During the course of further experiments it has been found that diffused daylight acts so rapidly in producing side-chain substitution that comparable results are only possible when light is rigidly excluded. On this account the comparative experiments described in this paper were carried out in the dark. In the second place, a much more rapid and accurate process for estimating the amount of the side-chain and nuclear substitution products was used in place of the former analytical method.

While these experiments were in progress several papers dealing with the closely related question of the bromination of toluene have appeared, and a review of the subject of the chlorination and bromination of benzene and toluene has been published by Bancroft in the third of a series of articles on "The Electrochemistry of Light" (*J. Physical Chem.*, 1908, **12**, 420).

When chlorine acts on toluene, side-chain substitution takes place (1) in sunlight at 0° and higher temperatures (*Schramm, Ber.*, 1885, **18**, 606); (2) in the dark at the boiling point of toluene. (*Cannizzaro, Compt. rend.*, 1855, **41**, 517). According to Häussermann and Beck (*Ber.*, 1892, **25**, 2445), side-chain substitution is greatly facilitated in the case of nitrotoluene in presence of sulphur. Sulphur thus appears to behave differently from the usual carriers, such as ferric chloride, molybdenum pentachloride, antimony pentachloride, iodine chloride, pyridine, and the aluminium-mercury couple, for these bring about nuclear substitution.

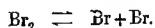
In contrast with the qualitative nature of the observations relating to the process of chlorination, quantitative measurements showing the influence of various factors on the side-chain and nuclear substitution have been obtained in connexion with the bromination of toluene. The experiments of Holleman, Polak, van der Laan, and Euwes (*Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 512; *Rec. trav. chim.*, 1908, **27**, 435), and those of Bruner and Dluska (*Bull. Acad. Sci. Cracow*, 1907, 693) have shown that the

relative proportion of bromine which enters the side-chain is not only increased by light, but in the dark it is increased by rise of temperature and by dilution of the reacting bromine. The methods adopted in these two series of experiments were not the same, for whereas Holleman and his collaborators used open vessels and only analysed the product obtained when the bromine had completely disappeared, Bruner and Dluska employed sealed tubes and analysed the products at different stages of the reaction.

The influence of the nature of the medium on the distribution of the bromine between the side-chain and the nucleus was also examined by these authors. When the toluene is considerably diluted by admixture with carbon tetrachloride, this distribution is the same as in the case of pure toluene, but dilution to the same extent with nitrobenzene has the effect of decreasing the proportion of the bromine which enters the toluene side-chain. This influence of the medium has been further studied by Bruner and Vorbrod (Bull. Acad. Sci. Cracow, 1909, 221), who investigated the effect of carbon disulphide, carbon tetrachloride, benzene, chloroform, acetic acid, benzonitrile, and nitrobenzene on the bromination of toluene, ethylbenzene, isopropylbenzene, and *o*-, *m*-, and *p*-xylene. They find that the influence of the solvent is not only observable in the dark, but shows itself in the process of photobromination. The effect of nitrobenzene, and to a less extent of acetic acid and benzonitrile, is greatly to diminish the proportion of side-chain substitution.

With regard to the bromination of toluene in the presence of carriers, Bruner and Holleman (*loc. cit.*) and Jackson and Field (*Amer. Chem. J.*, 1881, 2, 10) have found that side-chain substitution increases with decreasing concentration of the carrier and also with rise of temperature.

In explanation of these various observations, two essentially different views have been put forward. According to Bruner, side-chain substitution is due to molecular bromine, whereas nuclear substitution is effected by bromine atoms or ions, which result from the dissociation of bromine molecules in accordance with the equation:



The velocity measurements of Bruner and Dluska are cited as evidence in favour of this hypothesis. These determinations indicate that both the side-chain and nuclear substitution processes take place in accordance with the requirements of the equation for a unimolecular change if the concentration of the bromine is small. For higher bromine concentrations, the values obtained for the constant characteristic of a unimolecular change decrease as

the reaction proceeds. This is attributed to the withdrawal of active bromine from the solution by the formation of a hydrogen perbromide ( $\text{HBr}_2$ ). Since the dissociation of this perbromide increases as the concentration of the solution diminishes, its influence on the rate of progress of the bromination is inappreciable in the case of dilute bromine solutions.

According to this hypothesis, the action of carriers, such as iodine, consists in forming compounds with bromine which undergo dissociation with the production of bromine atoms or ions in much greater concentration than that which is obtained in the case of a pure solution of bromine. Hydrogen perbromide is supposed to be a dissociating compound of this character, and the increase in the proportion of nuclear substitution which is found when the toluene is mixed with nitrobenzene, benzonitrile, acetic acid, and certain other liquids, is attributed to the relatively large solubility of hydrogen bromide in these solvents, whereby the formation of hydrogen perbromides is facilitated.

Bruner's theory that nuclear substitution is due to ionic bromine is in the main adopted by Bancroft (*loc. cit.*). To account for certain observations, this author finds it necessary, however, to assume that nuclear substitution only occurs when negative bromine ions are present in excess of the corresponding positive ions. Such a condition is brought about by the partial combination of the positive bromine ions with molecular bromine to form complex positive ions, for example,  $\text{Br}_3^+$ .

The other view referred to is that put forward by Holleman, who supposes that side-chain substitution is due to molecular bromine, but that substitution in the nucleus is brought about by bromine in the form of hydrogen perbromide,  $\text{HBr}_2$ . Low temperature and increasing concentration of the solution are favourable to the formation of these polyhalogen compounds, and these are the conditions under which the proportion of nuclear substituted product increases. The fact that nitrobenzene and acetic acid, when added to the toluene, increase the relative amount of the nuclear substitution product, is obviously in agreement with this theory if the solubility relationships, referred to above, are taken into consideration.

An account will now be given of the observations which we have made in connexion with the chlorination of toluene, and the method of analysis of the chlorinated product may be described first.

This product consists of unchanged toluene, *o*- and *p*-chlorotoluene, and benzyl chloride. The benzyl chloride was extracted by Schultz's method (*Ber.*, 1884, 17, 1675), which consists in boiling a weighed quantity of the liquid with an excess of alcoholic

silver nitrate for fifteen to twenty minutes, and weighing the silver chloride. The method was tested with pure benzyl chloride and with benzyl chloride mixed with toluene and *o*- and *p*-chlorotoluene. The following results show that the method of estimation is satisfactory:

0.2618 benzyl chloride gave 0.2983 AgCl;  $C_6H_5\cdot CH_2Cl = 0.2639$ .  
0.8220 " " " 0.9192 AgCl;  $C_6H_5\cdot CH_2Cl = 0.8112$ .

The following mixtures were made and analysed:

	I.	II.	III.
Toluene .....	26.026	3.523	6.459
<i>o</i> -Chlorotoluene .....	9.323	1.329	4.8765
<i>p</i> -Chlorotoluene .....	5.306	1.267	2.0575
Benzyl chloride .....	4.845	2.103	2.3685

- I. 6.2013 gave 0.7055 AgCl;  $C_6H_5\cdot CH_2Cl = 10.04$ . Actual = 10.54 per cent.  
II. 3.0554 " 0.8815 AgCl;  $C_6H_5\cdot CH_2Cl = 25.46$ . " = 25.61 "  
III. 3.4065 " 0.5870 AgCl;  $C_6H_5\cdot CH_2Cl = 15.21$ . " = 15.03 "

The proportion of *p*-chlorotoluene in the mixture was estimated by oxidising the chlorinated product in a sealed tube at 115–120° for five to six hours with nitric acid (one part of acid, D 1.4, and two parts of water). The mixture of acids was collected and washed with cold water. The acids were then boiled with 200 c.c. of water for a few minutes, filtered hot, and washed with a small quantity of boiling water. All the benzoic and *o*-chlorobenzoic acid and a small quantity of *p*-chlorobenzoic acid are thus removed. It was found that one litre of boiling water dissolves about 1.0 gram of *p*-chlorobenzoic acid, so that a loss of approximately 0.20 gram of this acid has to be allowed for in the above method of separation. After washing as described, the acid was dried at 100° and weighed. The melting point of the acid was 234–235°. In carrying out this estimation of the *p*-chlorotoluene, it is necessary to keep the temperature at which the oxidation is effected as low as possible, for otherwise a portion of the *p*-chlorobenzoic acid may be decomposed. Mixtures of the following percentage composition were analysed by the above method:

	I.	II.
Toluene .....	19.16	15.73
<i>o</i> -Chlorotoluene .....	43.54	43.07
<i>p</i> -Chlorotoluene .....	19.40	20.92
Benzyl chloride .....	17.90	20.28

- I. 2.77 gave 0.695 *p* chlorobenzoic acid. *p*-Chlorotoluene = 20.3 per cent.  
II. 3.42 " 0.880 " " " = 20.8 "

In some of the earlier experiments, the total chlorine was determined by the Carius method. By deducting from this the chlorine present as benzyl chloride and *p*-chlorotoluene, the amount of *o*-chlorotoluene was obtained. In the later experiments this method

was replaced by a simpler and more rapid process involving the measurement of the density of the chlorinated product. If  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are the percentage amounts of toluene, *o*-chlorotoluene, *p*-chlorotoluene, and benzyl chloride respectively in a mixture of these substances, and if  $d_1$ ,  $d_2$ ,  $d_3$ , and  $d_4$  are the respective densities of these liquids (at 18°), we may obtain  $\alpha$  and  $\beta$  from the equations:

$$\alpha + \beta = 100 - \gamma - \delta \quad \dots \quad (1),$$

$$\frac{\alpha}{d_1} + \frac{\beta}{d_2} = \frac{100 - \gamma}{d} - \frac{\delta}{d_4} \quad \dots \quad (2),$$

in which  $d$  represents the density of the mixture. This method was applied in the analysis of the following mixtures:

		Percentage composition.		
		I.	II.	III.
Toluene .....	( $d_1 = 0.86791$ )	$\alpha = 19.90$	19.16	15.73
<i>o</i> -Chlorotoluene .....	( $d_2 = 1.08450$ )	$\beta = 30.90$	43.54	43.07
<i>p</i> -Chlorotoluene .....	( $d_3 = 1.07050$ )	$\gamma = 18.64$	19.40	20.92
Benzyl chloride .....	( $d_4 = 1.10271$ )	$\delta = 30.56$	17.90	20.28
Density of mixture .....		$d^{18} = 1.03615$	1.03584	1.04414
Calculated value of $\alpha$ (per cent.)		19.8	19.0	15.7

In calculating the above values of  $\alpha$ , the actual percentage amounts of *p*-chlorotoluene and benzyl chloride were assumed.

Having subsequently ascertained that the ratio of *p*- to *o*-chlorotoluene in the product of chlorination is nearly constant and equal to 1:2, the separate estimation of the para-compound was omitted in further experiments, and the total amount of the nuclear substitution product (*o*- + *p*-chlorotoluene) was alone determined. The density of a mixture of the two chlorotoluenes in the above ratio was found to be  $d^{18} = 1.0800$ . From this and the measured density,  $d$ , of a given mixture, we obtain the percentage amounts of toluene ( $\alpha$ ) and of the mixed chlorotoluenes ( $\beta + \gamma$ ) from the equations:

$$\alpha + (\beta + \gamma) = 100 - \delta \quad \dots \quad (3).$$

$$\frac{\alpha}{0.86791} + \frac{(\beta + \gamma)}{1.0800} = \frac{100}{d} - \frac{\delta}{1.10271} \quad \dots \quad (4).$$

The results obtained for a mixture of known composition by this method are indicated below:

		Percentage composition.
Toluene .....	$\alpha$	$\approx 92.20$
<i>o</i> - and <i>p</i> -Chlorotoluenes .....	$(\beta + \gamma)$	$= 3.75$
Benzyl chloride .....	$\delta$	$= 4.05$
Density of mixture .....	$d$	$= 0.88250$

1.8695 of the mixture gave 0.0868 AgCl, corresponding with  $\delta = 4.10$  per cent. of benzyl chloride. Substituting for  $\delta$  and  $d$  in equations (3) and (4), we obtained  $\alpha = 91.9$ ,  $(\beta + \gamma) = 4.0$  per cent. This example suffices to show that sufficiently accurate results for

the proportion of total nuclear substitution product in the mixture can be obtained by the indirect method of density determination. Previous to the carrying out of the above estimations, the chlorinated mixture was washed with a solution of sodium carbonate until the wash-water, acidified with nitric acid, gave no precipitate with silver nitrate solution. It was then dried over potassium carbonate.

*Variations in the Conditions of the Chlorination Process.*—In order to ascertain the influence of various factors on the distribution of the chlorine between the side-chain and the nucleus, the following series of experiments were made, the toluene in all cases being heated at its boiling point during the process of chlorination.

*Series I and II.*—Chlorination above a layer of hydrochloric acid solution (D 1.16) in the dark and in diffused daylight.

*Series III and IV.*—Chlorination with moist chlorine in the dark and in diffused daylight.

*Series V and VI.*—Chlorination with dry chlorine in the dark and in diffused daylight.

In the last four series of experiments hydrogen chloride was passed into the toluene with the chlorine, so as to make the conditions correspond as closely as possible with those of series I and II. In the experiments of series V and VI, the gases were passed through concentrated sulphuric acid and then over phosphoric oxide, and the toluene was freshly distilled over sodium.

The results of these experiments are given in table I, in which the last two columns of numbers represent respectively the percentage amounts of chlorine which enter the side-chain and the nucleus. The figures in the third column indicate the extent to which the chlorination was carried in the separate experiments. From a comparison of the individual results in the different series, it would appear that in some cases the distribution of the chlorine between side-chain and nucleus is to some extent dependent on the proportion of the toluene which is actually chlorinated. The variations are, however, not such as to permit of any definite conclusion in regard to this point, and we have considered it permissible to take the mean results of the separate experiments.

TABLE I.

*Chlorination with Ordinary Chlorine.*

Series.	Conditions.	Percentage of substitution products in final mixture.	Percentage of	
			Benzyl chloride.	<i>p</i> -Chloro- toluenes.
I. <i>a</i>	Layer of hydrochloric acid solution in the dark.	10	16	84
<i>b</i>		10	14.5	85.5
<i>c</i>		10	19	81
<i>d</i>		9	16	84
<i>e</i>		9	17	83
<i>f</i>		9	24	76
<i>g</i>		11	13.5	86.5
<i>h</i>		13	12.5	87.5
	Mean .....		16.5	83.5
II.	Layer of hydrochloric acid solution in the light.	17	64	36
		40	59	41
		48	56	44
	Mean .....		60	40
III.	Moist chlorine and hydrogen chloride in the dark.	12	63	37
		18	46	54
		8	76	24
		9	64	36
	Mean .....		62	38
IV.	Moist chlorine and hydrogen chloride in the light.	50	91	9
		35	90	10
	Mean .....		90	10
V.	Dry chlorine and hydrogen chloride in the dark.	29	91	9
		25	90	10
	Mean .....		90	10
VI.	Dry chlorine and hydrogen chloride in the light.	22	93.5	6.5
		44	94	6
	Mean .....		94	6

In reference to the experiments in series I, certain slight modifications were made in the experimental arrangement in order to ascertain whether the substituting effect of chlorine is influenced by previous exposure to light. In *a* and *b* the chlorine was exposed to the light of an arc lamp, focussed on the wash-bottle containing sulphuric acid, before it came into contact with the toluene. In *c*, *d*, *e*, and *f*, the chlorine was exposed to diffused daylight, the only difference being that in *e* the sulphuric acid in the wash-bottle was replaced by water. In *g* and *h*, the light of an ordinary incandescent electric lamp was allowed to act on the chlorine before it entered the toluene. Although the results of the several experiments vary to some extent, it is not possible to say that



the previous light treatment of the chlorine has any definite influence on the proportion of the side-chain substitution.

Before proceeding to compare the data in table I, it will be convenient to present the results of the experiments in which chlorination was effected by chlorine generated by electrolytic decomposition of a concentrated hydrochloric acid solution placed immediately below the toluene. The apparatus used was that described in the previous communication (*loc. cit.*), and, as in the other experiments, the temperature was maintained at the boiling point of toluene.

TABLE II.

*Chlorination with Electrolytic Chlorine.*

Series.	Conditions.	Percentage of substitution products in final mixture.	Percentage of	
			Benzyl chloride.	o- + p-Chloro-toluenes.
VII.	In the dark	0.5 amps., 8 hours	9	90.5
		0.5 " 24 "	3.5	94.5
		1 " 4 "	4	88.5
		1 " 4 "	7	91.5
		4 " 1 "	10	86.0
		4 " 2 "	21	88.0
Mean.....			10.0	90.0
VIII.	In the light	1 amp., 4 hours	59.0	41.0
		1 " 4 "	69.0	31.0
		Mean.....	64.0	36.0

Examination of table I shows that the influence of light on the ratio of distribution of the chlorine is very pronounced in the case where the reacting chlorine was passed through concentrated aqueous hydrochloric acid in contact with the toluene. The effect of insulation is to raise the proportion of chlorine which enters the side-chain from about 16 to 60 per cent. In the case where the moist gases were passed directly into the toluene, the effect of light is to raise the percentage of benzyl chloride from about 60 to 90. When, however, the dry gases are passed into dry toluene, the proportion of side-chain substitution product obtained in the dark is already so large that any considerable influence of light is impossible. As the numbers show, the effect of light in this case is very slight, the proportion of benzyl chloride being increased from 90 to 94 per cent.

If we compare series I, III, and V, which were all carried out in the dark, it is seen that the distribution of the chlorine is very largely dependent on the amount of water present. In the absence of water, the proportion of benzyl chloride amounts to 90 per cent.; when the chlorine and hydrogen chloride were not dried

before passing into the toluene, the mean of the divergent numbers obtained for the proportion of benzyl chloride is only 62 per cent., and when the toluene undergoing chlorination was saturated with water by contact with aqueous hydrochloric acid, the proportion of benzyl chloride is only 16 per cent. The considerable differences in the numbers for the separate experiments of series III may be due to the different amounts of moisture which were introduced by the undried gases in the different experiments.

The data obtained with electrolytic chlorine in the dark (series VII) must be compared with those of series I. The special arrangement adopted in this series was in fact designed to make the conditions as similar as possible to those which obtained in the process of electrolytic chlorination, and thereby to facilitate a comparison of the action of ordinary and electrolytic chlorine. The mean results of the two series are not identical, and it would appear that electrolytic chlorine gives rise to a somewhat smaller proportion of benzyl chloride than chlorine, which is obtained by the action of potassium permanganate on hydrochloric acid. In regard to this difference, it must, however, be noted that the conditions obtaining in the two series of experiments were not quite the same, for in the electrolytic chlorination, hydrogen was continuously evolved from one of the electrodes in the hydrochloric acid solution. It seems probable that the benzyl chloride, which must dissolve to a certain extent in the aqueous solution, is reduced by the nascent hydrogen, and this will result in a smaller proportion of benzyl chloride in the final product.

Series VIII, in which chlorination was effected by electrolytic chlorine in the light, must similarly be compared with series II. The mean values for the proportion of benzyl chloride are approximately the same, and it follows that the action of electrolytic chlorine is not sensibly different from that of ordinary chlorine.

Reference may here be made to the difference in the results which have now been obtained as compared with those communicated in the preliminary note (*loc. cit.*). In the earlier series of experiments, the conditions obtaining in the processes of electrolytic and ordinary chlorination were not sufficiently defined. The electrolytic experiments were made in a badly lighted room, whereas the ordinary chlorinations were effected in good daylight. This is largely responsible for the much greater differences which were found previously for the action of electrolytic chlorine on the one hand, and ordinary chlorine on the other. In the second place, the method previously employed in the analysis of the product of chlorination has been found to be unsatisfactory. This method involved the removal of unchanged toluene by distillation and the

oxidation of the residue by means of potassium permanganate. As indicated at the time, the oxidation of the chloro-substitution product by this method is very incomplete, and in the light of later results it appears that the readiness with which the different isomerides undergo oxidation is dependent on their relative proportions in the mixture examined.

The marked influence of moisture on the side-chain nuclear ratio is not peculiar to the chlorination process, for similar effects have been observed in experiments which we have made on the bromination of dry and moist toluene. The bromine used was allowed to remain for some days in contact with potassium bromide, then dried over fused calcium bromide, and distilled over barium oxide. The toluene was freshly distilled over sodium. Fifteen c.c. of a toluene solution, containing 7.2 per cent. by weight of bromine, were introduced into two blackened glass tubes, and 9 milligrams of water were then added to one of the tubes. The preparation of the bromine solution and the filling and sealing of the tubes were effected in a dark room by the aid of a feebly luminous gas flame. The sealed tubes were then placed in a closed box, immersed in a water-bath at 25°, until the bromine had completely disappeared. This occurred in the moist solution after fourteen days, and in the dry solution after thirty days. In a second experiment with a toluene solution containing 8.9 per cent. of bromine, to which in one case 39 milligrams of water were added, fourteen days elapsed before the disappearance of the bromine in the case of the moist solution, the corresponding period for the dry solution being about thirty-five days. The following table gives the relative amounts of side-chain and nuclear substitution products in these experiments:

TABLE III.

		Percentage of	
		Benzyl bromide.	Bromo- toluenes.
Experiment 1	{ Dry solution.....	27.8	72.2
	{ Moist " .....	18.7	81.3
Experiment 2	{ Dry solution.....	22.5	77.5
	{ Moist " .....	14.2	85.8

According to these data, the presence of water in the toluene reduces the proportion of benzyl bromide, and at the same time increases the rate at which the bromine disappears. The effect is therefore of the same kind as that observed in the chlorination experiments. On account of the wide differences in the conditions of the chlorination and bromination experiments, it is not, however, possible to make any quantitative comparison of the two series of data.

From a consideration of all the observations relating to the chlorination of toluene, it appears to be established that side-chain substitution is favoured by light, rise of temperature,\* and absence of moisture. In so far as these factors are concerned, the chlorination of toluene is influenced in the same way as the bromination process. The two processes would also appear to be similarly influenced by the nature of the medium, for when toluene, mixed with its own volume of nitrobenzene, was chlorinated, an increase in the relative proportion of the nuclear substitution product was observed. No data are available to show the influence of the concentration of the halogen in the case of the chlorination process, and on account of the limited solubility of chlorine in toluene at temperatures at which the reaction takes place, it is doubtful whether the influence of concentration could be experimentally determined with any accuracy.

Independently of the influence of the concentration of the halogen, it is clear that the degree of parallelism between the chlorination and bromination processes is such as to warrant the conclusion that the mechanism of the processes is of the same kind. The more extensive observations relating to the bromination of toluene may therefore be utilised in the elaboration of a general theory of halogenation.

Two theories relating to the special case of bromination have already been referred to in this paper. Both of these offer a plausible explanation of certain facts, but, on the whole, the view that nuclear substitution is due to halogen in the form of polyhalogen compounds appears to be the more acceptable. The diminution in the relative amount of nuclear substitution with rise of temperature and with diminishing concentration of the halogen is consistent with the polyhalogen theory, for both these factors are favourable to the dissociation of the polyhalides. The observed increase in the percentage of nuclear substitution product when certain solvents, such as nitrobenzene, benzonitrile, and acetic acid, are added to the toluene is in accord with the fact that these solvents facilitate the formation of polyhalogen compounds. Observations relating to polyiodides indicate that although these are formed to a small extent in hydrocarbons, carbon tetrachloride,

\* The influence of temperature on the nature of the product of chlorination is shown by experiments which were made with carefully dried materials at 0°. The relative amount of chlorine entering the side-chain was found to be 30 per cent. when chlorination took place in the dark and 45 per cent. when the experiment was conducted in the light. The corresponding numbers, obtained when the toluene was heated at its boiling point, are 90 and 94 per cent. respectively. These results show clearly enough the considerable influence of temperature both in the dark and in the light.

chloroform, and carbon disulphide, they are produced in very much larger quantities in nitrobenzene, ethyl acetate, benzonitrile, acetic acid, and certain other solvents. It is this particular property which appears to determine the nuclear substituting influence of these media.

That similar relationships hold in respect of the formation of polybromides is rendered probable by the results of distribution experiments which were made with carbon tetrachloride and nitrobenzene. According to Bruner and Dlnska (*loc. cit.*), the addition of carbon tetrachloride to toluene produces no alteration in the distribution of the bromine between the side-chain and the nucleus; it acts simply as a diluent, and as such reduces the velocity of the reaction.

Fifty c.c. of *N*-aqueous hydrobromic acid were shaken at 18° with 70 c.c. of carbon tetrachloride and of nitrobenzene respectively. After the liquids had been kept for an hour to allow of complete separation, 50 c.c. of the non-aqueous layer were titrated with 0.1*N*-sodium hydroxide. Less than 0.1 c.c. of alkali was required for neutralisation in the case of carbon tetrachloride, and less than 0.25 c.c. in that of nitrobenzene.

\* The same experiments were then made after the addition of bromine to the hydrobromic acid solution. The amount of bromine added was such that the composition of the resulting solution could be represented by 1.0*N* (HBr<sub>1.5</sub>). After shaking with this solution, 50 c.c. of each of the non-aqueous liquids were treated with potassium iodide and excess of sodium thiosulphate to remove bromine, and then titrated as before with 0.1*N*-alkali. The carbon tetrachloride required, as previously, less than 0.1 c.c. of alkali, whereas the nitrobenzene required 4.4 c.c., which is approximately twenty times \* as much as was required in the absence of bromine. These results show clearly the great difference between the two solvents in regard to the formation of polyhalogen hydrogen compounds.

It is possible that the relative stability of polyhalogen compounds in nitrobenzene solution is connected with the ionising power of this solvent, for the solutions of the polyiodides in nitrobenzene have been shown (Dawson and Gawler, *Trans.*, 1902, **81**, 525; Dawson and Jackson, *Trans.*, 1908, **93**, 2063) to be good conductors. Other solvents, like ethyl acetate and benzonitrile, which favour the formation of polyhalogen compounds and increase the relative amount of nuclear product in the bromination of toluene, also yield

\* The correct value of the acid ratio is probably very much greater than this, for a large proportion of the 0.25 c.c. of alkali required for titration in the absence of bromine, is due to the acid character of the nitrobenzene.

solutions which have a high electrical conductivity. Although there is no direct evidence to show that the nuclear substituting effect is conditioned by the ionisation, these facts would seem to indicate that halogen in the form of polyhalogen ion is specially active in this respect.

The fact that solutions of bromine and iodine in moist nitrobenzene are conductors of electricity (Bruner, *Bull. Acad. Sci. Cracow*, 1907, 731) is, at first sight, favourable to the view that nuclear substitution is due to free halogen ions. On the other hand, solutions of chlorine do not conduct (Bruner and Galecki, *Zeitsch. Elektrochem.*, 1910, 16, 204), and yet the processes of chlorination and bromination appear to be affected in a similar manner when the conditions of the two processes are similarly altered. These facts are difficult to reconcile with the ionic theory of nuclear substitution, and on this account we are inclined to adopt the polyhalogen theory.

Neither this nor the ionic theory appears to offer an immediate explanation of the fact that the presence of water in the toluene increases the relative proportion of the nuclear substitution products. Comparative measurements of the rate of leakage of electricity through dry and moist solutions of chlorine and hydrogen chloride in toluene were made in this connexion, but the results indicate that if there is any difference in the conductivity of the moist and dry solutions, it is not sufficiently large to account for the observed influence of moisture on the chlorination process on the assumption that nuclear substitution is due to chlorine ions. In so far as the resultant effects are concerned, the action of moisture is opposed to that of light, for this increases the rate of side-chain substitution, and the former accelerates the process of nuclear substitution. Before these catalytic effects can be explained, further experiments are necessary.

The question of carriers may finally be discussed. The assumption that the activity of these substances is due to an increase in the concentration of halogen ions as a consequence of the formation of more highly ionised "carrier-halogen" compounds is not, so far as we are aware, supported by any experimental evidence. On the other hand, if such "carrier-halogen" compounds are themselves of the nature of perhalogen compounds, or if they are capable of combining with further quantities of halogen to form such perhalogen derivatives, the formation of nuclear substitution products in the presence of carriers is explicable in terms of the polyhalogen theory without the necessity of formulating any additional electrolytic hypothesis. From a consideration of the valency relationships of the various substances which serve as

carriers, it seems likely that all these substances are capable of forming dissociating halogen addition compounds which belong to the polyhalogen type.

In the course of the above experiments, we have observed certain colour phenomena in connexion with the process of chlorination, which we propose to reserve for a further communication. When moist chlorine is passed into boiling toluene in the light, the toluene gradually assumes the yellow colour of chlorine. If, however, hydrogen chloride is passed in simultaneously, the yellow colour disappears, reappearing when the hydrogen chloride is cut off. In the dark the liquid retains its yellow colour in presence of hydrogen chloride. In some cases the chlorination product, after carefully washing free from chlorine and hydrogen chloride, retains a permanent pale yellow colour. The exact conditions which are necessary for the production of the colour change, which is probably due to the formation of a small quantity of a yellow-coloured substance, have not yet been determined.

THE UNIVERSITY,  
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### CLIII.—*The By-Products of Alcoholic Fermentation.*

By OLIVE EVELINE ASHDOWN and JOHN THEODORE HEWITT.

THE formation of small quantities of carbon compounds other than carbon dioxide and alcohol during the fermentation of various sugars by yeast has attracted much attention, and during the past few years considerable light has been thrown on the formation of some of these by-products. Whilst many endeavours have been made to solve the problem as to why and how succinic acid and the higher alcohols seem to be almost invariable constituents of crude alcohol, comparatively little attention has been devoted to the acetaldehyde which accompanies the alcohol in varying quantity, and which sometimes is formed in considerable amount.

If, however, one desires to throw light on the mechanism of the reaction by which alcohol is produced from dextrose and similar sugars, it is fairly evident that this substance is worthy of much greater attention, since whilst yeast normally produces alcohol with extremely small amounts of acetaldehyde, the fact that the latter substance is occasionally formed in much greater amount during abnormal fermentations is likely to lead to information of value if the nature of the abnormality is understood.

The occurrence of notable amounts of aldehyde might be referred to one of several possible causes:

Subsequent oxidation of alcohol by atmospheric oxygen. This hypothesis necessitates the presence of a catalytic agent, which might either be derived from an inanimate source, for example, some metallic salt the presence of which had been overlooked, or might be of an enzymatic nature and be derived from the yeast or some other organism.

2. The acetaldehyde may be produced from the sugar by a fermentation due to some other organism.

3. Sugars when fermented by yeast normally give ethyl alcohol and carbon dioxide, but owing to malnutrition of the yeast or some similar cause, acetaldehyde may make its appearance in place of ethyl alcohol to a greater or less extent.

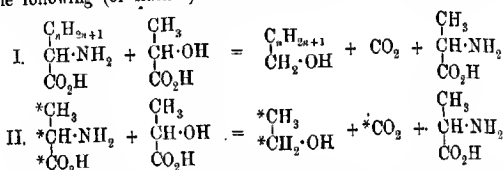
The first or second of these hypotheses may at first sight appear more probable, and one of the present authors at one time inclined to the view that the occurrence of larger amounts of aldehyde than usual was due to some agency outside the yeast. But, as will be seen later, the same yeast will give very varying amounts of acetaldehyde, according to the materials on which it is nourished being altered, other conditions remaining the same, so that the idea of the aldehyde being due to some other agency is out of the question. Moreover, the results obtained by the present authors with yeasts from different breweries show the same result, the production of aldehyde varying at different times with yeast from the same brewery, whilst any possibility of the aldehyde having been produced by subsequent catalytic oxidation owing to the presence of small amounts of salts of heavy metals was carefully excluded by performing all fermenting and distilling operations in glass vessels.

Evidently, then, the aldehyde must be a product derived from the sugar under the action of the yeast, the cause of the variation in amount being due to the different food the yeast is supplied with during fermentation. In order to obtain an idea as to which of the other constituents of the mash could affect the greater or lesser production of aldehyde, systematic experiments were carried out, solutions being made up of known composition. Generally, crystallised sucrose or dextrose was employed, together with necessary mineral constituents, nitrogen being also supplied either in the form of ammonium salts or as amino-acids. In view of the work of F. Ehrlich (*Zeitsch. Ver. deut. Zuckerind.*, 1905, **55**, 539; *Biochem. Zeitsch.*, 1906, **1**, 8; **2**, 52; *Ber.*, 1907, **40**, 1027, etc.) on the production of higher alcohols from the amino-acids with extra carbon atoms (for example, of ordinary isoamyl alcohol from leucine), complications were avoided by using alanine as amino-acid, since this can give no other alcohol but ethyl alcohol. In fact, the present authors started the work quite expecting to find

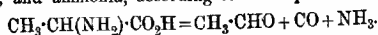


that deficiency in available nitrogen would mean increase in aldehyde content, and it was thought not at all unlikely that the function of amino-acids and their conversion into alcohols during fermentation might be connected with the formation of ethyl alcohol and carbon dioxide from some intermediate product, possibly lactic acid.

Assuming that lactic acid is formed as an intermediate product during the alcoholic fermentation of sugars, one might imagine the chemical change involved to be capable of representation in the following (or similar) manner:



That a plentiful supply of nitrogen in the form of ammonium salts or as alanine would reduce the amount of aldehyde to any appreciable extent was immediately negatived by the results obtained with a series of fermentations carried out on sucrose solutions to each of which equal amounts of potassium phosphate, magnesium sulphate, and calcium phosphate had been added, but which differed respectively in containing (a) no added nitrogenous material, (b) ammonium sulphate, (c) ammonium tartrate, and (d) alanine. A reference to table II, which records the results obtained with a Yorkshire yeast at the ordinary temperature (Jan., 1909) over a period of nineteen days, shows that whilst the largest yield of alcohol was obtained when alanine was added, and the next best yield with ammonium sulphate, least aldehyde was formed when the yeast had to depend on its own nitrogen, and the greatest amount (absolutely— the amount relatively to the alcohol formed was slightly greater in the case of ammonium tartrate) was produced when alanine was added. Evidently lack of nitrogenous food is not the cause of aldehyde formation, and a systematic search for ferments, whether inorganic or enzymic, which can effect a catalytic decomposition of alanine with production of acetaldehyde would seem desirable in view of the observation made by E. Drechsel (*Ber.*, 1892, 25, 3502), that alanine heated alone, or, still better, with an excess of concentrated phosphoric acid, to 220–230°, is decomposed into acetaldehyde, carbon monoxide, and ammonia, according to the equation:

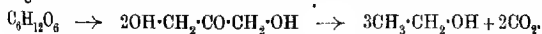


Drechsel draws particular attention to the wandering of an oxygen

atom of the carboxyl group (presumably the hydroxylic oxygen) to the  $\alpha$ -carbon atom, and it seems not unreasonable to suppose that, given a suitable enzyme, a similar transformation, resulting in the formation of acetaldehyde and formamide or ammonium formate, might be effected at the ordinary temperature.

During the progress of this work we fortunately turned our attention to a paper by H. Schade (*Zeitsch. physikal. Chem.*, 1906, 57, 1), who had discovered a method of fermenting dextrose to ethyl alcohol and carbon dioxide without the aid of any organism or organic enzyme. Briefly, this author found that dextrose is decomposed by alkalis with the formation of acetaldehyde and a formate, whilst acetaldehyde and formic acid yield ethyl alcohol and carbon dioxide under the influence of rhodium sponge. Schade thinks it not improbable that yeast effects the conversion of dextrose into ethyl alcohol and carbon dioxide in a somewhat similar manner, dextrose decomposing into an intermediate product, which in turn yields formic acid and acetaldehyde, an enzyme functioning in a similar manner to rhodium sponge then coming into play.

The nature of the intermediate compound which furnishes the acetaldehyde and formic acid (if the hypothesis of Schade is correct) is not quite clear; presumably the dextrose must first decompose to yield two molecular proportions of a compound,  $C_6H_{12}O_6$ , and perhaps the simplest assumption would be to regard this compound as lactic acid (compare Buchner and Meisenheimer, *Ber.*, 1904, 37, 417; 1905, 38, 620), which may furnish either ethyl alcohol and carbon dioxide directly, or else give acetaldehyde and formic acid, which may in turn react to give the end-products mentioned. It should, however, be noticed that a comparatively recent paper by P. Boysen Jensen (*Ber. Deut. bot. Ges.*, 1908, 26, A, 666) assumes that dihydroxyacetone is an intermediate product in the fermentation of dextrose to ethyl alcohol and carbon dioxide, for the oxime of this ketone is stated to have been isolated when hydroxylamine was added to a fermenting dextrose solution. Jensen consequently divides the fermentation of dextrose into stages:



and supposes that zymase consists of two enzymes, the first capable of effecting the conversion of dextrose into dihydroxyacetone, the second decomposing the latter into ethyl alcohol and carbon dioxide. He further states that an addition of glycerol inhibits the second reaction, so that in these circumstances dihydroxyacetone is isolated as the final product. This ketone may be decomposed by an oxydase, but in this case carbon dioxide and water are produced, no alcohol being formed.

Quite recently E. Buchner and J. Meisenheimer (*Ber.*, 1910, 43, 1773) have published the results of exhaustive experiments on the action of yeast, both living and as yeast juice, on a number of compounds containing a chain of these carbon atoms; their results are interpreted as disposing of the possible fermentation of lactic acid, methylglyoxal, or glyceraldehyde to ethyl alcohol and carbon dioxide, although with dihydroxyacetone and yeast juice, boiled yeast juice having been added (see A. Harden and W. Young, *Proc.*, 1905, 21, 189; E. Buchner and H. Haehn, *Biochem. Zeitsch.*, 1909, 19, 192), no less than 80 to 90 per cent. was fermented to alcohol and carbon dioxide. This result is even more striking than that of G. Bertrand (*Ann. Chim. Phys.*, 1904, [viii], 3, 257), who succeeded in fermenting 25 per cent. of this triose.

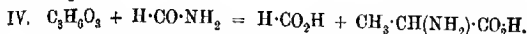
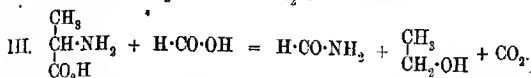
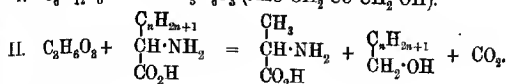
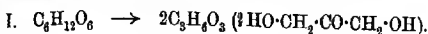
There seems to be a consensus of opinion that some intermediate product, probably of the formula  $C_3H_4O_3$ , is produced, and that this gives rise to alcohol and carbon dioxide either directly or possibly with the intermediate formation of acetaldehyde and formic acid, although Buchner and Meisenheimer consider Schade's view quite untenable (*Ber.*, 1906, 39, 4218; 1910, 43, 1782).

This objection is based on the negative results obtained in attempting to ferment a mixture of acetaldehyde and formic acid; of course, the harmful influence of these materials might be the cause of the enzyme being put out of action, but later experiments, in which yeast juice has been allowed to act on ethylidene oxide diacetate,  $[CH_3 \cdot CH(O \cdot CHO)]_2O$ , in which the aldehyde and formic acid are only produced slowly by a gradual hydrolysis, have proved no more successful.

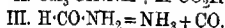
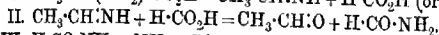
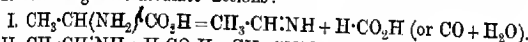
From these experiments of Buchner and Meisenheimer, it would appear that any possibility of formic acid playing a part in fermentation was out of the question, but, as our experiments show, the amount of acetaldehyde formed is largely reduced when a formate is present, whilst the use of small quantities of formic acid as an aid to good fermentations has been strongly advocated by H. Lange (*Zeitsch. f. Spiritusind.*, 1905, 28, 341).

It seems to us not improbable that some substance, possibly alanine, which should ferment normally to give ethyl alcohol and carbon dioxide, may be formed either as a product of the decomposition of the dextrose or perhaps as a transformation product of dihydroxyacetone in presence of nitrogenous material. Such a substance can give rise to acetaldehyde (Drechsel, *loc. cit.*); it may be that in presence of formic acid this latter reaction takes place to a more limited extent; certainly the fact remains that the presence of formates strongly diminishes the amount of acetaldehyde produced in alcoholic fermentation.

Without in any way committing ourselves to an explanation of the mechanism of the process, we think the following scheme may perhaps represent the course followed during the fermentation of dextrose to ethyl alcohol and carbon dioxide:



This represents small quantities of formic acid or formamide acting together with an enzyme of the yeast as catalytic agent; the occurrence of small amounts of one or other of these substances being quite possible in the light of Drechsel's work. In fact, the migration of oxygen from the carboxyl group to the  $\alpha$ -carbon atom in Drechsel's reaction can best be explained by the assumption of the following intermediate actions:



The first of these reactions will be observed to be fully analogous to the well-known decomposition of an  $\alpha$ -hydroxycarboxylic acid into an aldehyde and formic acid or its decomposition products. With reference to the possibility of formic acid playing a part in alcoholic fermentation, attention may be drawn to F. Ehrlich's views on the decomposition of leucine and the occurrence of valeraldehyde as a by-product (*Ber.*, 1907, 40, 1046).

The view now advanced, that dextrose decomposes into half-molecules (? dihydroxyacetone), and that these in turn furnish alanine under the action of small amounts of formamide, the alanine then reacting with formic acid under the influence of an enzyme to give ethyl alcohol and carbon dioxide with the regeneration of formamide, would gain much in probability if direct synthesis of  $\alpha$ -amino-acids from aldehydes and formamide were known; despite a careful search of chemical literature, we have found no synthesis of such a kind, and we are unfortunately prevented at the present time from carrying out a research in this direction. We may, however, sum up the arguments in favour of the suggested hypothesis.

1. The production of ethyl alcohol from alanine during fermentation by yeast brings the formation of the former substance

into line with that of its higher homologues from the higher amino-acids.

2. Acetaldehyde is always formed during the fermentation of dextrose by yeast; our experiments show that the quantity is in no way diminished by an increased supply of nitrogen, whilst Drechsel has shown that alanine yields acetaldehyde and the decomposition products of formamide (carbon monoxide and ammonia) on heating.

3. If alanine is an intermediate product of the conversion of dextrose into ethyl alcohol and carbon dioxide, the formation of lactic acid, which Slator\* regards as a by-product, is easily accounted for.

4. The hypothesis that formic acid and formamide play a part in the production of ethyl alcohol receives support from Schade's observation of the reaction between aldehyde and formic acid with rhodium as catalytic agent, and our experiments clearly show that with small quantities of formates initially present, the amount of acetaldehyde formed during fermentation is very markedly decreased.

We may incidentally draw attention to the greater amount of higher alcohols produced when no ammonium salts or alanine were added to the sugar solutions; seeing that in this case the yeast must draw on its own store of nitrogen with concomitant degradation of different amino-acids (leucine, etc., not merely alanine), one has a striking, if somewhat unnecessary, confirmation of Ehrlich's views as to the formation of the higher alcohols.

#### EXPERIMENTAL

The yeasts employed in these experiments were not pure cultures, but of known origin, and the authors desire to express their warm thanks to Messrs. J. L. Baker, A. R. Ling, and J. H. Millar for their kindness in supplying them with the necessary material. The usual procedure was to mix 5 grams of the pressed yeast with 10 c.c. of water, and add the resulting cream to a solution of 100 grams of sugar in 1 litre of water.

The use of solutions made up artificially with either sucrose or dextrose, potassium phosphate, magnesium sulphate, and calcium phosphate, and when nitrogenous material was also added, either alanine or ammonium sulphate or tartrate, was preferred to the employment of beer wort, as a complete check on the material

\* Lactic acid seems to be out of the question as the intermediate product between dextrose and ethyl alcohol and carbon dioxide. See A. Slator, *Trans.*, 1906, 83, 141; 1908, 93, 231; *Ber.*, 1907, 40, 123; and E. Buchner and J. Meisenheimer, *Ber.*, 1910, 43, 1776, 1785.

supplied to the yeast was thus obtained. The solutions were made with boiling water, and subsequently aerated, but any access of air during the fermentation was excluded, owing to the necessity of connecting the Winchester-quart bottles in which the operation was conducted with washing tubes, so that all the escaping carbon dioxide passed through about 50 c.c. water to retain any aldehyde or other vapour carried off by the stream of gas. It is probable that the lack of aeration explains the somewhat small yield of alcohol obtained in many cases. In some experiments fermentation was allowed to proceed at the prevailing temperature, in others the temperature was maintained at 30°. In the latter case all the Winchester-quart bottles of one set of experiments were immersed in the same water-bath, so that temperature conditions should be strictly comparable.

At the end of a fermentation experiment, the contents of the bottle and the attached washing-tube were transferred to a flask and distilled with the aid of a rod-and-disk stillhead furnished with a thermometer; the distillation was always allowed to proceed several minutes after the temperature-reading had shown that water alone was passing over, thus ensuring that all volatile by-products were carried over in the current of steam. A second distillation was usually resorted to in order to concentrate the alcohol sufficiently for the necessary estimations. It is scarcely necessary to remark that considerable pains were exercised in cooling the vapours; the end of the condenser passed into a flask through a cork, which also carried a long reflux tube, so as to ensure volatile constituents being retained.

Besides estimating alcohol in the distillates, the amounts of volatile acid, esters, aldehyde, and higher alcohols were also determined; furfuraldehyde proved to be absent or present only in indeterminable traces. The estimations of the secondary constituents were carried out essentially according to the methods recommended by Girard and Cuniassé (*Manuel pratique de l'Analyse des Alcools et des Spiritueux*, Paris, 1899), and since comparative results were chiefly desired, the colorimetric method for estimating the higher alcohols, using an isohutyl alcohol standard, was adopted. Both in this case and in estimating the acetaldehyde colorimetrically, several standard solutions were always employed, and the colour developed was matched against the nearest standard. In this way much of the uncertainty experienced in using two liquids of very different intensity of colour was avoided.

The lack of any very close connexion between the supply of nitrogen and the amount of aldehyde produced is shown by the set of experiments recorded in table I.

TABLE I.

Five grams of Yorkshire yeast, stirred up with 10 c.c. of water, were added to each of five solutions. Each of these five solutions contained 200 grams of sucrose, 10 grams of potassium phosphate, 10 grams of magnesium sulphate, and 1.0 gram of calcium phosphate (for added nitrogenous material see the table itself). The yeast was added on Jan. 6th, 1909, the temperature maintained at 30° for sixty-six hours, and, after a further sixty-five hours at 10–15°, the fermented liquids were distilled on Jan. 11th.

None of the results are good as regards alcohol production; the temperature employed was unsuitable for the yeast in question; the highest yield of alcohol was, however, obtained when nitrogenous material was added in the form of alanine. The much greater production of higher alcohols where the yeast had merely its own nitrogen to depend on (experiment 2) is very noticeable.

Experiment .....	1.	2.	3.	4.	5.
Added nitrogenous material.	16 grams ammonium sulphate.	None.	20 grams alanine.	30 grams ammonium tartrate.	20 grams ammonium tartrate.
Yield of alcohol (in grams)	66.2	35.4	67.5	33.5	42.8

By-products; expressed as grams per 100 litres of absolute alcohol.

Acids .....	—	27.1	30.3	53.8	41.4
Esters .....	—	45.7	19.4	55.2	72.5
Aldehydes .....	71.3	52.5	53.2	81.3	66.1
Higher alcohols .....	120.0	255.2	141.0	44.4	80.0

TABLE II.

In another set of experiments, using exactly the same materials and some of the same sample of yeast, but where the fermentation was allowed to proceed at the ordinary temperature for nineteen days (Jan. 6th to 25th, 1909), much better yields of alcohol were obtained.

Experiment .....	1.	2.	3.	4.	5.
Added nitrogenous material.	16 grams ammonium sulphate.	None.	20 grams alanine.	30 grams ammonium tartrate.	20 grams ammonium tartrate.
Yield of alcohol (in grams)	80.7	41.2	84.75	52.4	56.0

By-products; expressed as grams per 100 litres of absolute alcohol.

Acids .....	40.6	29.1	23.3	45.4	30.5
Esters .....	67.3	34.1	63.3	76.0	67.0
Aldehydes .....	28.2	6.9	84.3	86.0	91.3
Higher alcohols .....	34.2	38.2	—	14.7	46.0

The amounts of alcohol produced under these more favourable conditions as to temperature are considerably larger; the small amount obtained in experiment 2 is only to be expected, the yeast

being starved with regard to nitrogen. The particular experiment is instructive, so small an amount of aldehyde having been produced, a result with which we were much surprised at the time, as we thought the increased production of aldehyde probably depended on the yeast obtaining insufficient nitrogenous food. It is also interesting that the absolutely largest quantity of aldehyde was produced when alanine was supplied.

TABLE III.

In order to control the foregoing results, experiments were made using dextrose solutions and fermenting with a London beer yeast at 30°. Each solution contained 100 grams of dextrose (crystallised, colourless), 5 grams of potassium phosphate, 5 grams of crystallised magnesium sulphate, and 0.5 gram of calcium phosphate in 1 litre of water. To each solution 5 grams of yeast, stirred up with 10 c.c. of water, were added on Jan. 28th, 1909, and the solutions were distilled on Feb. 2nd.

Experiment .....	1.	2.	3.
Added nitrogenous material .....	8.0 grams ammonium sulphate.	None.	10.0 grams ammonium tartrate.
Alcohol produced (in grams).....	37.8	31.8	40.9
Grams of aldehyde per 100 litres alcohol	50.0	13.1	51.8

Again the small yield of alcohol where no nitrogenous material was added is noticeable, and, as before, least aldehyde was also formed. The yeast from experiment 2 was therefore used to ferment a fresh dextrose (100 grams) solution (in 1 litre of water), salts being added as before, and also 10 grams of ammonium tartrate. 39.4 Grams of absolute alcohol were then obtained, and the aldehyde figure had risen to 41.0. In this experiment fermentation proceeded for ninety hours at 30°.

Thus there can be no doubt that a plentiful supply of nitrogen, instead of diminishing the aldehyde, rather tends to increase the amount produced. We, consequently, in the light of Schade's work, turned our attention to the influence of formates on the production of aldehyde, and found that the quantity was considerably reduced; instead of 30 to 90 parts of aldehyde per 100,000 of absolute alcohol, numbers from 5 to 20 (sometimes more) were usually obtained. The amounts of sodium formate employed were much larger than necessary in our earlier experiments (1 to 9 in table IV), so that occasionally slightly more aldehyde was produced when 10 instead of 5 grams of sodium formate were employed to 100 grams of sucrose, the excess material being probably without much influence.



TABLE IV.

In the following four sets of experiments, in each separate experiment a solution was made up with 100 grams of sucrose, 5 grams of potassium phosphate, 5 grams of magnesium sulphate, and 0.5 gram of calcium phosphate to 1 litre of boiling water. The amount and form in which nitrogen was added or not is shown in the table. After cooling, the solutions were aerated, and 5 grams of yeast stirred up with 10 c.c. water added in each case.

In experiments 1 to 5 a beer yeast was added on March 13th, 1909, and a temperature of 30° was maintained for about ninety hours (see table). Experiments 6 to 9 were started on the same day with some of the same yeast, but fermentation was allowed to proceed at the prevailing laboratory temperature until March 25th.

In experiments 10 to 17 a porter yeast was added on May 5th, 1909, the temperature was kept at 30° for three days, and fermentation stopped after a further two days at the laboratory temperature.

A beer yeast was again employed for experiments 18 to 25, the fermentation was started on June 3rd, 1909, the temperature maintained for two days at 30°, and the fermentation stopped after a further two days at the laboratory temperature.

The results recorded in the following table demonstrate the far larger amounts of aldehyde usually produced when formates are absent, and evidently comparing the first nine experiments with the succeeding ones, quantities of sodium formate ranging from 5 to 10 per cent. of the weight of the sucrose are quite unnecessary. Turning to the strictly comparable set of experiments 10 to 13, the increasing amount of aldehyde with the decreasing amount of sodium formate is very noticeable; in another strictly comparable set, namely, 22 to 25, exactly the same phenomenon is noticed. In set 14 to 17, slight irregularities are observed, but here in each case the aldehyde-content was fairly low, and the same remark applies to experiments 18 to 21, in which, compared with the other three experiments, No. 18 has given a somewhat anomalous result.

The record of the determinations of volatile acids (calculated as acetic acid) and esters (as ethyl acetate) has been given, but although care was taken to obtain all the alcohol and by-products produced, no attempt was made to get all the distillates of the same alcoholic strength, or time given to allow the equilibrium:

$$\text{alcohol} \times \text{acid/ester} \times \text{water} = \text{a constant}$$

to be attained, so that varying ratios of acids to esters are not to be wondered at.

# THE BY-PRODUCTS OF ALCOHOLIC FERMENTATION. 1647

Expt.	Duration of fermentation.	Temperature.	Other materials added to solution (grams).				By-products; grams per 100 litres absolute alcohol.			
			Sodium formate.	Ammonium sulphate.	Ammonium tartrate.	Alcohol produced (grams)	Acids.	Esters.	Aldehyde.	Higher alcohols.
1	88 hours	30°	5	8	—	41·4	37·4	67·5	16·7	75·8
2	90½ "	30	10	8	—	45·6	22·4	77·9	22·0	139·0
3	91½ "	30	5	—	—	45·3	20·8	61·0	50·0	90·9
4	92½ "	30	10	—	—	45·1	12·4	67·5	3·8	33·65
5	95½ "	30	10	—	10	47·5	12·7	99·5	20·5	64·8
6	12 days	15	5	8	—	45·6	22·8	58·1	40·6	71·4
7	12 "	15	10	8	—	47·6	14·5	91·0	33·0	70·9
8	12 "	15	5	—	—	36·2	17·1	100·2	21·9	182·0
9	12 "	15	10	—	—	37·3	14·5	113·2	29·0	100·0
10	{ 3 "	30 }	2	8	—	43·0	23·3	150·0	11·1	58·8
	{ 2 "	15 }								
	{ 3 "	30 }								
11	{ 2 "	15 }	0·5	8	—	46·0	33·2	88·0	15·6	105·0
	{ 3 "	30 }								
12	{ 2 "	15 }	0·1	8	—	42·7	67·4	98·8	41·7	160·0
	{ 3 "	30 }								
13	{ 2 "	15 }	0	8	—	41·2	58·9	88·4	53·2	140·0
	{ 3 "	30 }								
14	{ 2 "	15 }	2	—	—	43·9	18·9	85·0	24·1	180·0
	{ 3 "	30 }								
15	{ 2 "	15 }	0·5	—	—	41·9	26·9	73·2	30·0	130·0
	{ 3 "	30 }								
16	{ 2 "	15 }	0·1	—	—	43·5	11·4	48·4	11·4	129·0
	{ 3 "	30 }								
17	{ 2 "	15 }	0	—	—	41·0	13·6	46·1	14·75	165·0
	{ 3 "	30 }								
18	{ 2 "	15 }	2	8	—	37·2	33·5	129·0	24·0	70·8
	{ 3 "	30 }								
19	{ 2 "	15 }	0·5	8	—	43·3	32·4	190·3	8·8	30·2
	{ 3 "	30 }								
20	{ 2 "	15 }	0·1	8	—	39·4	60·6	228·6	20·0	95·2
	{ 3 "	30 }								
21	{ 2 "	15 }	0	8	—	37·0	56·5	162·6	23·7	74·1
	{ 3 "	30 }								
22	{ 2 "	15 }	2	—	—	33·6	23·7	46·1	24·6	79·4
	{ 3 "	30 }								
23	{ 2 "	15 }	0·5	—	—	32·5	18·1	122·3	27·4	76·9
	{ 3 "	30 }								
24	{ 2 "	15 }	0·1	—	—	30·8	14·7	109·1	32·0	99·0
	{ 3 "	30 }								
25	{ 2 "	15 }	0	—	—	32·5	14·5	—	51·3	191·0
	{ 3 "	30 }								

The yields of alcohol, as we have previously mentioned, are far from ideal, but it has to be remembered that after the first aeration following the making up of the solutions, the fermentations were carried on without any access of air, and in some cases there is no doubt that an insufficient supply of nitrogen contributed to lack of vigour on the part of the yeast. This is well seen by comparing experiments 8 and 9 (mean amount of alcohol 36·7 grams) with 6 and 7 (47·1 grams), or experiments 22 to 25 with 18 to 21.

We think, however, our experiments conclusively show that the amount of aldehyde is markedly diminished by the presence of formates during fermentation, and although Schade's original theory as to the rôle played by formic acid in fermentation may need modification, it should not too lightly be set on one side.

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CLIV.—*The Absorption Spectra of Furan, Furfuraldehyde, Thiophen, and Pyrrole under Different Conditions.*

By JOHN EDWARD PURVIS.

IN this communication an account is given of a comparative study of the absorption spectra of furan, furfuraldehyde, thiophen, and pyrrole, as vapours at various temperatures and pressures, in solution and as liquids, in order to ascertain the nature and extent of the selective absorption under these various conditions.

The apparatus employed has been already described in previous communications (this vol., pp. 692, 1035). The substances were distilled several times before being used. Not much furan was available, so that only two series of observations of the vapour at increasing temperatures and pressures were possible; and none were taken at decreased pressures. Alcoholic solutions of the substances were, however, examined, in order to compare them with those of furfuraldehyde.

TABLE I.

*Furan.*—The absorption bands in furan vapour at various temperatures and pressures in a column 100 mm. long. Barometric pressure = 749 mm.

Abbreviations: w. = weak; v.w. = very weak; str. = strong; narr. = narrow; f.wide = fairly wide; f.w. = fairly weak; mod. str. = moderately strong.

13°. 749 mm.	30°. 793 mm.	45°. 819 mm.
λ.	λ.	λ.
2652 w., wide	2652 w., wide	2652 w., wide
2647 "	2647 "	2647 "
2642 "	2642 "	2642 "
2637 f.wide, w.	2637 f.wide, w.	2637 f.wide, w.
2634 " str.	2634 " str.	2634 " str.

13° 749 mm.	30° 783 mm.	45° 819 mm.
$\lambda$ . 2630 narr., w. 2627 f.wide, w. 2620 wide, w. 2601 narr., w. 2599 " 2593 f.wide, w. 2589 head of strong band, sharp on more re- frangible side. 2541 f.wide, w. 2539 " 2530 head of strong band, sharp on more re- frangible side.	$\lambda$ . 2630 narr., w. 2627 w., f.wide 2620 w., wide 2601 w., narr. 2599 " 2593 f.wide, w. 2589 head of strong band 2541 w., f.wide 2538 " 2530 head of strong band	$\lambda$ . 2630 w., narr. 2627 w., f.wide 2620 w., wide 2601 w., narr. 2599 " 2593 f.wide, w. 2589 head of strong band 2541 w., f.wide 2538 " 2530 head of strong band
The rays were then trans- mitted to Cd 2265, but they were very weak be- tween 3370 and Cd 2329.		

15 bands.

15 bands.

15 bands.

60° 849 mm.	75° 879 mm.	90° 909 mm.
$\lambda$ . { 2652 w. 2647 w. 2642 w. 2637 w. 2634 f.w. 2630 w. 2627 w. 2620 w. 2601 w. 2599 w. 2593 w. 2589 mod.str. 2541 } v.w., only just 2538 } visible 2530 }	$\lambda$ . { 2652 v.w. 2647 " 2642 " 2637 " 2634 " 2630 " 2627 " 2620 " 2601 " 2599 " 2593 " The rays were then trans- mitted to about 2560, and general absorption after that.	No bands were seen; and general absorption from 2700, the strong Cd line 2573 being just visible.
The rays were then trans- mitted to about 2590; the Cd lines 2329, 2321, 2313, and 2288 were just visible.		

15 bands.

11 bands.

No bands.

The effect of increasing the temperatures and pressures was not to show up any new bands, but the bands noticed at 13° and 749 mm. pressure were slightly wider and stronger at the increased temperatures and pressures. The bands at 2589 and 2530 were very similar in appearance, as were also 2634 and 2627. The three weak bands 2652, 2647, and 2642 were similar, and differ in their wave-lengths by about 5 units. The bands 2541, 2530, and 2599, 2589 form a group differing by equal wave-lengths.

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Besides that, the bands can be considered as a whole, and show differences of wave-lengths, for example:

2652			
15	2647		
2637	13	2642	
10	2634	12	mean = 14
2627	14	2630	
28	2620	15	mean = 13
2599	27	2601	
58	2593		
2541	55	2589	
	2538	59	mean = 57 = 13.5 × 5
		2530	

The numbers should be read diagonally, and from left to right.

TABLE II.

*Furfuraldehyde*.—The absorption bands in furfuraldehyde vapour at various temperatures and pressures in a column 100 mm. long.

Abbreviations: w.=weak; narr.=narrow; sh.=sharp; f.str.=fairly strong; v.w.=very weak; str.=strong.

17°. 763 mm.	30°. 807 mm.	45°. 833 mm.
λ. { 2726 w., narr., sh. 2725 narr., sh., stronger than 2726 2720 w., narr. 2718 " 2712 f.str. 2709 stronger than 2712 2706 w., narr. 2704 stronger than 2706 2701 w., narr. 2699 " 2697 "	λ. { 2726 w., narr. 2725 w., wider than at 17° 2720 " 2718 " 2712 " 2709 " General absorption began at λ 2700.	λ. { 2726 2725 General absorption began at λ 2720. 2 bands. 60°. 863 mm. λ. No bands. General ab- sorption began at λ 2730.
11 bands.	6 bands.	No bands.
75°. 893 mm.	90°. 923 mm.	100°. 939 mm.
λ. No bands. General ab- sorption began at λ 2740.	λ. No bands. General ab- sorption began at λ 2748.	λ. No bands. General ab- sorption began at about λ 2743.

TABLE III.

The absorption bands in furfuraldehyde in a column 100 mm. long at a constant temperature of 12° and under varying pressures. Abbreviations as in table I.

8 mm.	153 mm.
$\lambda$ . { 2721 v.w. { 2718 " { 2712 " { 2709 " { 2706 " { 2704 " { 2702 " { 2698 w. { 2696 stronger than 2698 { 2688 str. { 2681 f.w. { 2679 stronger than 2681 { 2676 w. { 2674 stronger than 2676 { 2668 w. { 2666 stronger than 2668 { 2660 { 2654 w. { 2652 stronger than 2654 { 2641 w. { 2639 stronger than 2641	$\lambda$ . The same series of bands were visible as at 8 mm. pressure; the chief difference was that the Cd lines 2573 to 2194 were weaker.  21 bands.   303 mm. $\lambda$ . The same series of bands were visible as at 8 mm. and 153 mm. pressure but the Cd lines from 2573 to 2194 were weaker.  21 bands.

General absorption began at  $\lambda$  2620; the Cd lines 2573, 2329, 2321, 2313, 2288, 2265, 2194, and 2144 were visible.

21 bands.

453 mm.	608 mm.	733 mm.
$\lambda$ .	$\lambda$ .	$\lambda$ .
{ 2721 v.w.	{ 2721 v.w.	{ 2721 v.w.
{ 2718 "	{ 2718 "	{ 2718 "
{ 2712 "	{ 2712 "	{ 2712 "
{ 2709 "	{ 2709 "	{ 2709 "
{ 2706 "	{ 2706 "	{ 2706 "
{ 2704 "	{ 2704 "	{ 2704 "
{ 2702 "	{ 2702 "	{ 2702 "
{ 2698 w.	{ 2698 "	{ 2698 "
{ 2696 w.	{ 2696 "	{ 2696 "
{ 2688 w.	{ 2688 "	{ 2688 "
{ 2681 w.	{ 2681 "	
{ 2679 w.	{ 2679 "	
{ 2676 w.		
{ 2674 w.		

General absorption at  $\lambda$  2650; the Cd lines 2573 to 2144 were very weak.

General absorption from  $\lambda$  2670; the Cd lines from 2573 to 2144 were very weak.

General absorption from  $\lambda$  2680; the Cd line 2573 was just visible, and the Cd lines from 2329 to 2194 were only just visible.

TABLE IV.

The absorption bands of furfuraldehyde in a column 100 mm. long at a constant temperature of 100° and under varying pressures. Abbreviations as in table I.

6 mm.	156 mm.	306 mm.
$\lambda$ .	$\lambda$ .	$\lambda$ .
{ 2676 v.w.	{ 2702 v.w.	{ 2712 v.w.
{ 2674 "	{ 2698 "	{ 2709 "
{ 2668 "	{ 2696 "	{ 2706 "
{ 2666 "	{ 2688 "	{ 2704 "
{ 2593 w., wide	{ 2681 "	{ 2702 "
{ 2589 "	{ 2679 "	{ 2698 "
{ 2530 "	{ 2676 "	{ 2696 "
	{ 2674 "	{ 2686 "
	{ 2668 "	{ 2681 "
	{ 2666 "	{ 2679 "
	{ 2660 "	{ 2676 "
	{ 2654 "	{ 2674 "
	{ 2652 "	{ 2666 "
	{ 2641 "	{ 2666 "
	{ 2639 "	{ 2660 "
	{ 2593 "	{ 2654 "
	{ 2589 "	{ 2652 "
	{ 2530 "	

The rays were then transmitted to Cd 2194.

General absorption from  $\lambda$  2420, the Cd lines from 2329 to 2194 being visible.

General absorption from  $\lambda$  2650, the Cd 2673 and the Cd lines from 2329 to 2144 being visible.

7 bands.	16 bands.	17 bands.
456 mm.	608 mm.	736 mm.
$\lambda$ .	$\lambda$ .	$\lambda$ .
{ 2721 v.w.	{ 2721 v.w.	No bands. General absorption from $\lambda$ 2720.
{ 2718 "	{ 2718 "	
{ 2712 "	{ 2712 "	
{ 2708 "	{ 2709 "	
{ 2706 "	{ 2706 "	
{ 2704 "	{ 2704 "	
{ 2702 "	{ 2702 "	
{ 2696 "		
{ 2696 "		

General absorption from  $\lambda$  2694; the Cd lines 2329 to 2194 were just visible.

General absorption from 2700.

9 bands. 7 bands.

The distinguishing features of the vapour of furfuraldehyde were that at the lower pressures the bands were sharper and slightly narrower than at the higher pressures, and that more bands were visible. Also, that the bands occur chiefly in groups of two, the distances of the constituents being about 2 units, and that they became wider and wider as the wave-lengths decrease; for example,

$\lambda$  2696 was slightly wider and stronger than  $\lambda$  2698;  $\lambda$  2679 was wider and stronger than  $\lambda$  2681. Besides that, if we consider these groups amongst themselves, they become wider as the wave-lengths decrease; for example, the members of the group 2641—2639 were wider than those of 2698—2696, but they were not so strong; and if the bands are considered as a whole, most of them show fairly even differences of wave-lengths, as the following arrangement indicates:

2726			2718		
24	2725		30	2712	
2702	27	2721	2688	31	2709
34	2698	25	34	2681	30
2668	32	2696	2654	2679	30
	2666	36	61	2652	33
		2660	2593	63	2641
				2589	2639
					2704
					30
					2674

*Thiophen*.—Pauer (*Wied. Ann.*, 1897, 61, 363) found that no bands were observed in the vapour of thiophen in a tube 100 mm. long, and that general absorption began at about  $\lambda$  2460.

The author has examined the vapour of thiophen in a column 200 mm. long, and has discovered a few bands.

TABLE V.

The absorption bands of thiophen in a column 200 mm. long at various temperatures and pressures. Abbreviations as before.

20°.	30°.	45°.
761 mm.	805 mm.	831 mm.
$\lambda$ .	$\lambda$ .	$\lambda$ .
2590 w., narr.	2590 w., narr.	2590 w.
2530 "	2530 "	2530 w.
2500 w., wide		
General absorption began at $\lambda$ 2490.	General absorption began at $\lambda$ 2500.	Both these bands are wider than at 30° and 761 mm. General absorption began at $\lambda$ 2505.
3 bands.	2 bands.	2 bands.
60°.	70°.	90°.
861 mm.	891 mm.	921 mm.
$\lambda$ .	$\lambda$ .	$\lambda$ .
2599 w.	No bands. General absorption began at $\lambda$ 2640, Cd 2573 being visible.	No bands. General absorption began at $\lambda$ 2720.
2599 w.		
Both bands are a little wider than at 45° and 831 mm. General absorption began at $\lambda$ 2520.		
2 bands.	No bands.	No bands.



TABLE VI.

The absorption bands of thiophen vapour in a column 200 mm. long at a constant temperature of 15° and under varying pressures.

14 mm.		164 mm.		314 mm.	
$\lambda$ .		$\lambda$ .		$\lambda$ .	
No bands.	General absorption began at $\lambda$ 2420.	No bands.	General absorption began at $\lambda$ 2460.	2690 v.w.	2530 „
				General absorption at $\lambda$ 2470.	
No bands.		No bands.		2 bands.	
464 mm.		614 mm.		744 mm.	
$\lambda$ .		$\lambda$ .		$\lambda$ .	
2590 v.w.		2590 w.		2590 w.	
2530 „		2530 w.		2530 w.	
General absorption at $\lambda$ 2470.		Both bands stronger than at 464 mm. General absorption at $\lambda$ 2490.		Both bands stronger than at 614 mm. General absorption at $\lambda$ 2500.	
2 bands.		2 bands.		2 bands.	

The vapour of thiophen was also examined in a column 100 mm. long at a constant temperature of 14° and under varying pressures. The three weak bands described in table V were not seen; but three wide bands were observed in the more refrangible regions which are hidden by the general absorption in the 200 mm. tube.

TABLE VII.

The absorption bands of thiophen vapour in a column 100 mm. long at a constant temperature of 14° and under varying pressures.

14 mm.		164 mm.		460 mm.		744 mm.	
$\lambda$ .		$\lambda$ .		$\lambda$ .		$\lambda$ .	
2416 wide band, about 0.5 A.U.		2416 wide „		2415 wide		2415 wide	
wide		2406 „		2406 „		2406 „	
2406 wide band, about 0.7 A.U.		2395 „, stronger than at 14 mm.		2395 „		2395 „	
wide		Absorption of rays from $\lambda$ 2375 to Cd 2329; the Cd lines		Absorption of rays from $\lambda$ 2375 to Cd 2329.		General absorption began at $\lambda$ 2390, the Cd lines 2329 to 2265 being visible.	
2395 wide, w.		from 2329 to 2239 were visible.					
Absorption of rays from $\lambda$ 2390 to Cd 2329, Cd lines 2321 to 2265 well marked.							
3 bands.		3 bands.		3 bands.		3 bands.	

From the above tables relating to thiophen vapour, it will be noticed that in the 200 mm. tube at the higher temperatures and pressures two weak and rather narrow bands were observed at 2590 and 2530, and that in the 100 mm. tube these bands were

too weak to be seen, but three wide weak bands were visible, which were covered by the general absorption of the greater mass of vapour in the 200 mm. tube.

TABLE VIII.

*Pyrrrole.*—The absorption bands of pyrrrole in a column 200 mm. long at a constant temperature of 17.5° and under varying pressures. Abbreviations as before.

746 mm.	466 mm.	166 mm.	16 mm.
λ.	λ.	λ.	λ.
2590 w.	2590 w.	2590 v.w.	All the rays were transmitted to λ 2265; the Cd lines 2194 and 2144 visible.
2530 w.	2530 w.	2530 "	
2495 w., wide	2595 w., wide	2495 "	
2481 "	2481 "	2481 "	
		2470 "	
General absorption from λ 2475.	General absorption from λ 2460.	General absorption from λ 2440.	
4 bands.	4 bands.	4 bands.	No bands.

The vapour was also examined in a column 200 long at a constant temperature of 100° and under pressures varying from 16 mm. to 746 mm., but no bands were observed.

The above table shows the presence of two narrow weak bands at 2590 and 2530, and three weak wide bands at 2495, 2481, 2470, in the vapour of pyrrrole.

#### Solutions.

*Puran.*—Hartley and Dobbie (Trans., 1898, 73, 598) examined alcoholic solutions of varying strengths, but they found no absorption bands. The author has examined alcoholic solutions of different strengths, and through varying thicknesses, but no bands were observed. The following numbers represent the positions where general absorption began through various thicknesses of the solutions.

N/10-solution:	2 mm. thick:	general absorption began at λ 2300.
30 "	" "	" "
N/100-solution:	2 "	" "
30 "	" "	" "
N/1000-solution:	2 "	" "
30 "	" "	" "
	50 "	" "
	" "	" "

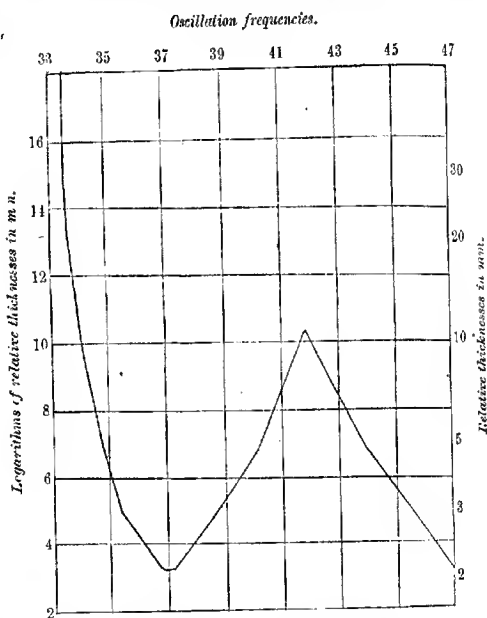
*Furfuraldehyde.*—Hartley and Dobbie (*loc. cit.*) stated that alcoholic solutions did not exhibit any absorption bands. When 0.096 gram was dissolved in alcohol, general absorption began at λ 3087 through 1 mm. thick, and at λ 3723 through 25 mm. thick.

The author examined N/10- and N/100-solutions, but no bands

were observed, and the following numbers represent the positions where general absorption began:

N/10-solution:	2 mm. thick:	general absorption began at $\lambda$ 8120.
30 "	" "	" " " " $\lambda$ 8590.
N/100 solution:	2 "	" " " " $\lambda$ 2870.
30 "	" "	" " " " $\lambda$ 3160.

In examining a N/1000-solution, however, a large band was discovered, the absorption curve of which has been drawn (Fig.).



N/1000 solution of furfuraldehyde in alcohol.

*Thiophen.*—Hartley and Dobbie (*loc. cit.*) found that there were no bands in any of the alcoholic solutions they used, but that the latter were very transparent. The author has examined the following solutions, but no bands were observed:

N/10 solution:	2 mm. thick:	general absorption began at $\lambda$ 2500.
30 "	" "	" " " " $\lambda$ 2560.
N/100-solution:	2 "	" " " " $\lambda$ 2460.
30 "	" "	" " " " $\lambda$ 2510.
N/1000-solution:	2 "	" " " " $\lambda$ 2195.
30 "	" "	" " " " $\lambda$ 2470.

*Pyrrole.*—Hartley and Hobbie (*loc. cit.*) found no bands in any of the alcoholic solutions of varying strengths and thicknesses that they employed. Coblentz (*Astrophys. J.*, 1904, **20**, 207) found a band in the ultra-red regions of the spectrum at  $2.94\mu$ . The author has examined alcoholic solutions of various strengths, but no bands were observed in the ultra-violet.

N/10 solution:	2 mm. thick:	general absorption began at $\lambda$ 2380.				
	30 "	"	"	"	"	$\lambda$ 2645.
N/100 solution:	2 "	"	"	"	"	$\lambda$ 2295.
	30 "	"	"	"	"	$\lambda$ 2425.
N/1000 solution:	2 "	"	"	"	"	$\lambda$ 2195.
	30 "	"	"	"	"	$\lambda$ 2325.

*Liquids.*—The liquids furfuraldehyde and pyrrole were also examined. For this purpose, a drop of the liquid was pressed between two thin quartz plates, and held in front of the slit of the spectroscope, whilst the light of the Cd spark was passed through for five minutes. No bands were observed, and the regions where general absorption began were:

	$\lambda$ .
Furfuraldehyde .....	3130
Pyrrole .....	2320
Thiophen (Pauer) .....	2540

#### General Results and Discussion.

The more important results of the preceding investigations are that:

(1) The vapour of furan exhibits absorption bands, some of which are very similar in appearance and have similar differences in wave-lengths. The vapour of furfuraldehyde exhibits bands, most of which can be grouped together in having similar differences both in appearance and in wave-lengths, but which are different from those of furan. The vapours of thiophen and pyrrole show a few bands, two of which are comparable with two in the vapours of furan and furfuraldehyde.

(2) Alcoholic solutions of various strengths of furan, thiophen, and pyrrole show no absorption bands, whilst N/1000-solution of furfuraldehyde exhibits a strong band in the ultra-violet. The liquids, furfuraldehyde, thiophen, and pyrrole, have no absorption bands.

The author has already compared and discussed the results of a comparative study of the vapours, liquids, and solutions of various substances (*loc. cit.*). The present investigation confirms generally the conclusions that the selective absorption by the molecules of any substance is conditioned, not only by the type and orientation of the atoms, but also by the physical conditions, as vapours, liquids, or in solution.

With regard to the solutions, it is remarkable that furan, pyrrole, and thiophen are so transparent, and that furfuraldehyde exhibits so large a band. The many bands found in the vapour of the latter substance disappear, and their place is taken by one large band. The comparative transparency of the vapours of pyrrole and thiophen, on the other hand, is comparable with that of the solutions. The possible influence of the solvent on the vibrations of dissolved molecules, as well as the absence of bands in liquids, has been discussed in the previous papers (*loc. cit.*).

Considering the vapours, it is clear that the vibrations of the atoms of the furan molecule are wholly different from those of the thiophen and pyrrole molecules. The substitution of oxygen by sulphur or the NH-group has completely altered the oscillations or vibrations which produce selective absorption. The thiophen and pyrrole vapours are transparent as compared with furan and furfuraldehyde, and there are only two bands common to them all. The series of phenomena may be compared by considering the influence of the oxygen atom on the vibrations of the other atoms of the ring. The oxygen atom appears to be the controlling influence, for the vapours of furan and furfuraldehyde have a considerable number of bands; and these bands are absent, with two exceptions, from the vapours of thiophen and pyrrole, in which the oxygen atom is replaced by sulphur and the NH-group respectively. In this direction the results may be discussed from the point of view of valency, and how far the changing valencies of sulphur and nitrogen are responsible for the remarkable absence of bands in the vapours of thiophen and pyrrole, as compared with furan and its aldehydic derivative. In the case of furan and its derivative the normal valency of oxygen is saturated, and the vapours exhibit a considerable number of bands, whereas in thiophen and pyrrole the valencies of the sulphur and nitrogen atoms are not saturated, and there are only a few bands in the vapours of these substances. Considering a single molecule of furan, and assuming the saturation of the valency of the oxygen atom to be normal and complete, the molecule would be more stable, more elastic, and more frequently periodic in its vibrations, because its energy may be considered to be wholly contained within the single system. On the other hand, in pyrrole or thiophen, the energy would not be wholly contained within the molecule, because the valency of the sulphur or the nitrogen atom is not at its maximum saturation. Part of the energy is employed externally to the single molecular system, and, as a result, the molecule does not possess the stability or the elasticity of the furan molecule; the regular periodicity of its vibrations is small in com-

parison, and the bands are fewer in number and generally different in position.

Nevertheless, it is not sufficient to explain satisfactorily the differences in the absorption bands from valency considerations alone. For example, Baker and Baly (Trans., 1907, 91, 1122) explained the absence of bands in the ultra-violet regions of solutions of piperidine by considering the saturation of the various atoms; but, as the author has pointed out (this vol., p. 692), the presence of the many bands in the vapour of piperidine is opposed to such an explanation. Nor is it sufficient to isolate any particular atom, or group of atoms, in a molecule, and consider these alone as the primary agents in any vibrations producing selective absorption. The introduction of a single atom in a molecule must affect the movements of all the atoms; and the vibrations of all the atoms are concerned in the final result. The forces which influence these lie both inside and outside the molecule. They include such factors as valency, mass, the nature of the ring system and its side-chains, and the physical conditions as vapours or in solutions; and, in view of the corpuscular theory of the atom, a complete explanation of the origin of selective absorption implies a consideration of many and deep-seated factors.

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the greater part of the cost of the apparatus employed in this investigation was defrayed.

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#### CLV.—*The Oxidation of Monohydric Phenols with Hydrogen Peroxide.*

By GEORGE GERALD HENDERSON and ROBERT BOYD, B.Sc.  
(Carnegie Research Scholar).

HAVING occasion to prepare some dihydric phenols of the formula  $C_{10}H_{12}(OH)_2$ , we endeavoured to find a simpler and more direct method of obtaining these compounds from monohydric phenols than those which are usually employed. To begin with, we applied to thymol the process of oxidising monohydric phenols in alkaline solution with potassium persulphate, which is stated to work well with the lower members of the series, but the results were not satisfactory. Equally disappointing results attended our trials of

the method of oxidation with dilute solutions of hydrogen peroxide, but the use of Merck's "perhydrol," a 30 per cent. aqueous solution of hydrogen peroxide, led to the attainment of the desired end. A number of monohydric phenols of the benzene series were treated with this reagent, glacial acetic acid being used as a solvent for the phenol, and all were found to undergo oxidation more or less easily, either in the cold or when moderately heated. The product was either a quinone, from which, of course, the corresponding dihydric phenol could be obtained by reduction, or a dihydric phenol, or, in one or two cases, a tetrahydric phenol. The following is a statement of the phenols examined and of the products obtained from them under the conditions described below.

Thymol gave a very good yield of thymoquinone, along with a small quantity of a new tetrahydric phenol, *tetrahydroxycymene*,  $C_6MePr^3(OH)_4$ , a colourless, crystalline solid, melting at  $168^\circ$ .

Carvacrol gave the same products as thymol, in approximately the same relative proportions.

3:5-Diethylphenol,  $C_6H_3Et_2 \cdot OH$ , gave, apparently as sole product, the corresponding 3:5-diethyl-*p*-benzoquinone,  $C_6H_3Et_2O_2$ , golden-yellow needles, melting at  $36^\circ$ , from which, by reduction with sulphurous acid, the dihydric phenol, 3:5-diethylquinol,  $C_6H_3Et_2(OH)_2$ , was obtained in colourless crystals, melting at  $114^\circ$ . *p*-Nitroso-3:5-diethylphenol was also prepared. It forms pale yellow crystals, melting at  $136^\circ$ , and on reduction and subsequent oxidation yields diethyl-*p*-benzoquinone.

*p*-tert.-Butylphenol,  $C_6H_4(CMe_3) \cdot OH$ , gave a new tetrahydric phenol, *tetrahydroxy-tert.-butylbenzene*,  $C_6H(CMe_3)(OH)_4$ , which crystallises in slender, colourless needles, melting at  $138^\circ$ .

Phenol gave quinol, a little *p*-benzoquinone, and a little catechol; no resorcinol was found.

*o*-Cresol gave toluquinol (2:5-dihydroxytoluene) and some toluquinone; *m*-cresol gave toluquinol, some toluquinone, and a little orcinol; and *p*-cresol gave homocatechol (3:4-dihydroxytoluene); no other product was found.

The character of the oxidation products obtained depended, in the first place, on the constitution of the phenol oxidised, and, in the second place, on the conditions of the experiment, namely, the proportion of perhydrol used, the concentration of the acetic acid solution, the temperature, and the time. As regards the first point, it was found that monohydric phenols, in which the *p*-position relative to the hydroxyl radicle is unoccupied by a radicle other than hydrogen, are more or less easily attacked by hydrogen peroxide even at the ordinary temperature, and that the product of oxidation is mainly a quinone, or a *p*-dihydric phenol, or a mixture

of both, according to the conditions under which the reaction is carried out. On the other hand, those monohydric phenols in which the *p*-position relative to the hydroxyl group is occupied are oxidised with greater difficulty, and a higher temperature is necessary; in such cases the product is usually a dihydric phenol containing the hydroxyl groups in the *o*-position with respect to each other. The lower members of the series tend to give tarry products more easily than the higher members, and it is best to use a larger proportion of the solvent (acetic acid) when the former are being oxidised.

We have also examined the action of perhydrol on some cyclic hydrocarbons. In each case the hydrocarbon was mixed with perhydrol, sufficient acetic acid to form a clear solution was added, and the liquid was left for some time at the ordinary temperature or gently heated. The members of the benzene series which were used, namely, benzene, toluene, 1:3-diethylbenzene, and cymene, did not appear to react at all easily with the oxidising agent, but naphthalene, anthracene, and phenanthrene were readily oxidised, yielding phthalic acid, anthraquinone, and phenanthraquinone respectively.

The course of the preparative work involved in this investigation led us to attempt to prepare higher dihydric phenols directly by condensing quinol and resorcinol with diethyl ether in presence of anhydrous aluminium chloride. These experiments were unsuccessful, but we found that phenol could be condensed with methyl propyl ether, yielding a substance which appears to be a *methylpropylphenol*,  $C_6H_5MePr-OH$ .

We intend to continue to study the behaviour of hydrocarbons towards perhydrol, and also to extend our experiments to derivatives of phenols and to phenols other than those of the benzene series.

#### EXPERIMENTAL.

According to a patented process (D.R.P. 81068 and 81298), dihydric phenols of the benzene series can be obtained on the manufacturing scale from monohydric phenols by means of potassium persulphate. The persulphate is added in small portions to a dilute alkaline solution of the phenol, and the liquid is kept for one or two days at the ordinary temperature, or at 40°. When the reaction is finished, the solution is saturated with carbon dioxide, any unchanged phenol is distilled off in a current of steam, the residual liquid is acidified with dilute acid and then boiled, and finally the dihydric phenol which has been formed is extracted with ether. If the *p*-position relative to the hydroxyl group in the monohydric phenol is free, a *p*-dihydroxy-compound is obtained,



but if the *p*-position is occupied, the product contains two hydroxyl groups in the *o*-position with respect to each other. Thus, phenol yields quinol, whilst *p*-cresol yields homocatechol.

As the process appeared to be a practicable one, we applied it in the prescribed manner to the oxidation of thymol, but found that with that compound the reaction does not proceed smoothly, as in the case of lower phenols. Much of the thymol remained unattacked, whilst the rest was mainly converted into a tarry substance, from which it was scarcely possible to separate any definite oxidation product. Various modifications of the process were tried—such as keeping the mixture cool with ice; adding the persulphate to a solution of thymol in the least possible quantity of alkali, and maintaining the mixture slightly alkaline by addition of sodium carbonate from time to time; agitating a mixture of thymol with aqueous potassium persulphate for several days, both at the ordinary temperature and at 60°—but with no improvement in the results.

A dilute solution of hydrogen peroxide, either with or without the addition of a small quantity of an iron salt, has frequently been used as an oxidising agent, and, according to Martinon (*Bull. Soc. chim.*, 1885, [ii], 43, 155), when dilute aqueous hydrogen peroxide is gradually added to pure phenol in the cold, and the liquid is subsequently heated to 90°, oxidation of the phenol takes place, and a mixture of quinol, *p*-benzoquinone, and catechol is obtained. With thymol, however, we found this process also to be unsatisfactory; using ordinary "ten volume" hydrogen peroxide, according to Martinon's method, very little of the thymol was attacked, even when the mixture was heated. It then occurred to us to try a stronger solution of hydrogen peroxide, and this led to success. It was found that thymol and other monohydric phenols, when dissolved in glacial acetic acid, are more or less readily oxidised by perhydrol, with the results described in the following pages.

*Oxidation of Thymol with Perhydrol.*—Seventy-five grams of thymol (1 mol.) were mixed with 190 c.c. of perhydrol (about 2 mols.), sufficient acetic acid was added to hold the thymol in solution, and the mixture was kept at the ordinary temperature. After a week or two, a small quantity of a colourless, crystalline solid had separated from the solution. The solid was collected, and water was gradually added to the filtrate until no further precipitation took place. The yellow, crystalline precipitate was agitated with dilute sodium hydroxide, when only a small part passed into solution, and the undissolved portion was collected, washed with water, and dried. The golden-yellow crystals obtained in this way melted at 45.5°, and were identified as thymoquinone.

A small additional quantity of thymoquinone was obtained from the mother liquor by steam distillation. Only a little of the thymol remained unoxidised.

The alkaline solution with which the thymoquinone had been washed gave, on acidification, a precipitate of a crystalline compound, which proved to be identical with the substance which had crystallised from the original acetic acid solution. After purification by recrystallisation from dilute alcohol, it was dried and analysed:

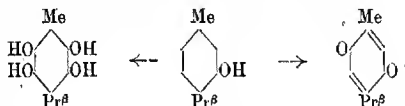
0.1562 gave 0.3460  $\text{CO}_2$  and 0.0947  $\text{H}_2\text{O}$ .  $\text{C} = 60.4$ ;  $\text{H} = 6.7$ .

0.1544 „ 0.3399  $\text{CO}_2$  „ 0.0992  $\text{H}_2\text{O}$ .  $\text{C} = 60.1$ ;  $\text{H} = 7.1$ .

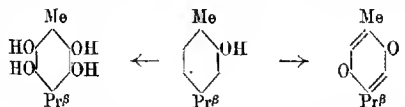
$\text{C}_{10}\text{H}_{14}\text{O}_4$  requires  $\text{C} = 60.6$ ;  $\text{H} = 7.1$  per cent.

*Tetrahydroxycymene*,  $\text{C}_6\text{MePr}^\beta(\text{OH})_4$ , so obtained, forms small, colourless crystals, which melt at  $168^\circ$ . If exposed to the air in a moist state, it begins to turn yellow. It is rather sparingly soluble in cold water, readily so in alcohol, ether, chloroform, or glacial acetic acid. It dissolves with ease in solutions of alkali hydroxides, and the colourless liquid quickly begins to acquire a brown coloration in contact with air. In an aqueous solution, ferric chloride produces a bulky, red precipitate.

The chief product of the oxidation of thymol by perhydrol is thymoquinone, whilst tetrahydroxycymene is only formed in small proportion. Very little tarry matter is produced.



*Oxidation of Carvacrol with Perhydrol.*—The oxidation was carried out in the same way as in the case of thymol, and, as was to be expected, the result was precisely similar. The chief product was thymoquinone, and, in addition, a small quantity of tetrahydroxycymene was formed. Only a little tarry matter was produced, and almost all the carvacrol was oxidised.



*Oxidation of 3:5-Diethylphenol with Perhydrol.*—The diethylphenol required for this experiment was prepared by Jannasch and Rathjen's method (*Ber.*, 1899, **32**, 2392), which gave a satisfactory yield.

The diethylphenol was oxidised with perhydrol in the same way as thymol. When the reaction appeared to be completed, the

solution was diluted with water, and the yellow crystals, which separated after some time, were collected and purified by crystallisation from dilute alcohol. Examination of the properties of the compound showed it to be 3:5-diethyl-*p*-benzoquinone,  $C_8H_8Et_2O_2$ , which, for purposes of comparison, we had already prepared by another method described below. The filtrate was neutralised with sodium carbonate and agitated with ether, the ethereal solution was washed and dried, and after removal of the ether by distillation a dark red, oily residue was obtained. The oily substance was shaken up with water, and after a short time the greater part solidified. The crystals were collected and drained on a porous plate, and, after recrystallisation, proved to be a further quantity of diethyl-*p*-benzoquinone. The small quantity of oily matter which was produced along with the quinone was not further examined.



Diethyl-*p*-benzoquinone was also prepared from diethylphenol by a less direct method.

*p*-Nitroso-3:5-diethylphenol,  $O_2C_6H_3Et_2NOH$  (diethyl-*p*-benzoquinoneoxime), was first obtained as follows. Diethylphenol was dissolved in alcohol previously saturated with hydrogen chloride, the solution was cooled with ice, and a cooled concentrated aqueous solution of the calculated quantity of sodium nitrite was slowly added. The dark green liquid obtained in this way was poured into water, when a yellowish-brown solid was precipitated. The precipitate was collected, washed with water, dried, washed with a little chloroform, and recrystallised from dilute alcohol. It forms small prisms of a pale yellow colour, which melt and decompose at  $136^\circ$ . It is readily soluble in alcohol, and almost insoluble in water:

0.1940 gave 13 c.c.  $N_2$  at  $15^\circ$  and 760 mm.  $N=7.84$ .

0.3920 „ 26.4 c.c.  $N_2$  at  $20^\circ$  and 760 mm.  $N=7.7$ .

$C_{10}H_{13}O_2N$  requires  $N=7.8$  per cent.

3:5-Diethyl-*p*-benzoquinone,  $O_2C_6H_3Et_2$ , was prepared from nitrosodiethylphenol in the following manner. Five grams of the nitroso-compound were dissolved in 50 grams of 10 per cent. ammonia, and the solution was saturated with hydrogen sulphide. The reduction product, *p*-aminodiethylphenol, was precipitated as a white solid, which was collected and washed with water. The precipitate was dissolved in 90 c.c. of 3 per cent. sulphuric acid, and 100 c.c. of water and 50 c.c. of a 10 per cent. solution of potassium dichromate were added. After about half an hour, the precipitate

which had formed was collected and dissolved in glacial acetic acid, and small quantities of chromic anhydride were added to the solution from time to time until the oxidation was completed. The quinone was then precipitated with water, collected, washed with water, and purified by crystallisation from dilute alcohol. It forms slender needles of a golden-yellow colour, which melt at  $36^{\circ}$ . If it is allowed to separate slowly from solution, crystals several centimetres in length may be obtained. It is only slightly soluble in water, but easily so in alcohol or ether, and it volatilises readily in a current of steam:

0.1967 gave 0.5294  $\text{CO}_2$  and 0.1240  $\text{H}_2\text{O}$ .  $\text{C}=73.4$ ;  $\text{H}=7.0$ .

$\text{C}_{10}\text{H}_{12}\text{O}_2$  requires  $\text{C}=73.2$ ;  $\text{H}=7.3$  per cent.

The corresponding dihydric phenol, 3:5-diethylquinol,  $\text{C}_8\text{H}_8\text{Et}_2(\text{OH})_2$ , was prepared by reduction of the quinone with sulphurous acid. The quinone was gently warmed with aqueous sulphurous acid until all the solid had passed into solution, and the reduction appeared to be completed. The phenol was then extracted with ether, and the ethereal solution was washed with water, dried, and concentrated to small bulk. On cooling, the phenol separated in small, colourless crystals. It melts at  $114^{\circ}$ , and is fairly easily soluble in water, and readily so in alcohol or ether. A solution in alkali hydroxides is at first colourless, but quickly turns brown on exposure to air. In aqueous solution the phenol is readily oxidised by ferric chloride, yielding the quinone:

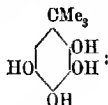
0.2707 gave 0.7145  $\text{CO}_2$  and 0.2073  $\text{H}_2\text{O}$ .  $\text{C}=72.0$ ;  $\text{H}=8.6$ .

$\text{C}_{10}\text{H}_{14}\text{O}_2$  requires  $\text{C}=72.3$ ;  $\text{H}=8.4$  per cent.

*Oxidation of p-tert-Butylphenol,  $\text{C}_6\text{H}_4(\text{CMe}_3)\cdot\text{OH}$ , with Perhydrol.*—The phenol required for this experiment was prepared from *tert*-butylbenzene. Nitration of the hydrocarbon yielded a mixture of the solid *p*- with some of the liquid *o*-nitro-derivative. The *p*-nitro-compound was separated and reduced by means of tin and hydrochloric acid. The oily *p*-amino-compound was diazotised, and on distilling the solution with steam, a satisfactory yield of the phenol was obtained in lustrous needles, which melted at  $98^{\circ}$  (compare Studer, *Ber.*, 1881, 14, 1472).

Five grams of the phenol were mixed with 10 grams of perhydrol and the quantity of acetic acid required to form a clear solution. In this case the reaction appeared to proceed very slowly at the ordinary temperature, hence the solution was heated at about  $60^{\circ}$  for several days, and then neutralised with sodium carbonate and agitated with ether. The ethereal solution was washed with water, dried, and after removal of the ether by distillation, a white, solid residue was left, which was recrystallised from dilute alcohol. The substance thus obtained was found on analysis to be tetrahydroxy-

tert. butylbenzene,  $C_6H(CMe_3)(OH)$ . It crystallises in slender, colourless needles, which melt at  $133^\circ$ . It dissolves rather sparingly in water, but freely in alcohol or ether and in solutions of alkalis. Ferric chloride does not produce a coloration in an aqueous solution. The probable constitution of the compound is shown by the formula



0.1179 gave 0.2602  $CO_2$  and 0.0764  $H_2O$ .  $C=60.2$ ;  $H=7.2$ .

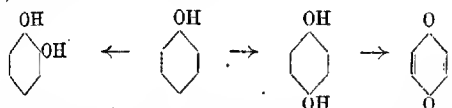
$C_{10}H_{14}O_4$  requires  $C=60.6$ ;  $H=7.1$  per cent.

From the mother liquor from which the tetrahydric phenol had crystallised, a small quantity of another colourless, crystalline compound was isolated. This substance melts at  $58^\circ$ , and is sparingly soluble in water, but readily so in solutions of alkalis. There was, however, too little in our hands for identification. Not much tarry matter was formed, and practically all the butylphenol was oxidised. We expected to get a dihydric phenol (3:4-dihydroxybutylbenzene) as the chief product, but probably the fact that the mixture was heated for some time accounts for the formation of the more highly oxidised compound. A repetition of the experiment at a lower temperature may yield the dihydric phenol.

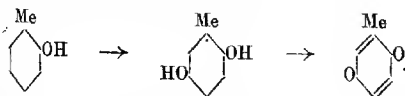
Having obtained these results with phenols of the formula  $C_{10}H_{13}OH$ , it appeared of interest to investigate the behaviour towards perhydrol of some of the lower members of the series, and we selected as examples phenol and *o*-, *m*-, and *p*-cresols. Preliminary experiments showed that these compounds are more susceptible to the action of the oxidising agent than thymol and the other higher phenols examined, and that in order to prevent the formation of considerable quantities of tarry matters it was necessary to avoid using excess of perhydrol, to dilute the mixture with a larger proportion of acetic acid, and usually to carry out the oxidation at the ordinary temperature.

*Oxidation of Phenol with Perhydrol.*—The phenol was mixed with perhydrol in such quantity that about 1 mol. of hydrogen peroxide was present for each mol. of phenol, and about twice the quantity of acetic acid necessary to keep the phenol in solution was added. After keeping for several days at the ordinary temperature, a crop of crystals had separated from the solution. The solid was collected, purified, and proved to consist of quinol, by determination of its melting point,  $169^\circ$ , and by its easy conversion into *p*-benzoquinone by oxidation with ferric chloride in aqueous

solution. The liquid from which the crystals of quinol had been removed was distilled with steam, when a little *p*-benzoquinone passed over and was collected. The residual liquid gave a precipitate when mixed with lead acetate. The first portion of the precipitate, which was very impure, was rejected; the rest was collected and decomposed with dilute sulphuric acid. The filtrate from the lead sulphate was agitated with ether, and from the ethereal solution a solid which gave all the reactions of catechol was obtained. A further quantity of quinol was obtained from the liquid from which the lead salt of catechol had been separated, but no resorcinol could be detected. Thus, with the strong solution of hydrogen peroxide, the oxidation products from phenol were the same as those obtained by Martinon (*loc. cit.*) by the use of a dilute solution:

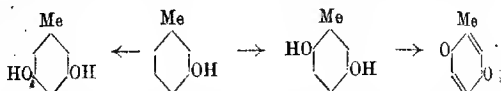


*Oxidation of o-Cresol with Perhydrol.*—The conditions of the experiment were the same as in the case of phenol, except that as the oxidation proceeded much more slowly at the ordinary temperature, the liquid was heated to 60° for two days, with the result that a considerable proportion of tarry matter was formed. The liquid was then distilled in a current of steam, and, along with some unchanged *o*-cresol, there passed over a yellow, crystalline compound, which was identified as toluquinone. The residual liquid was neutralised with sodium carbonate and agitated with ether, and from the ethereal solution, after washing with water and removal of the ether, a dark-coloured, oily residue was obtained. This residue was dissolved in water, and the tarry impurities were precipitated by addition of lead acetate; the filtrate was then found to contain toluquinol. No other oxidation products could be detected with certainty, although it is not improbable that the lead precipitate contained a little of such:

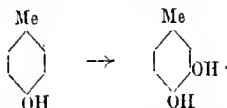


\* *Oxidation of m-Cresol with Perhydrol.*—The oxidation was carried out precisely as in the case of phenol. After being kept for a sufficient time, the liquid was distilled in a current of steam, and the distillate was found to contain toluquinone, together with some unchanged *m*-cresol. The residual liquid was filtered in order

to remove some tarry matter which was present, lead acetate was added to the filtrate, and the lead salt, which was precipitated, was collected. The filtrate was agitated with ether, and toluquinol was obtained on concentration of the ethereal extract. The lead salt was decomposed with dilute sulphuric acid, and the filtrate from the lead sulphate yielded to ether a substance with the reactions of orcinol:



*Oxidation of p-Cresol with Perhydrol.*—Preliminary experiments showed that *p*-cresol was not oxidised by perhydrol nearly so easily as *o*- or *m*-cresol, and consequently the mixture of *p*-cresol, perhydrol, and acetic acid was heated at about 60° for three days. The greater part of the acetic acid was then neutralised with sodium carbonate, and the oily liquid which was thrown out of solution was separated. The aqueous liquid gave no precipitate with lead acetate, which indicated the absence of *isocresinol*. It was agitated with ether, and after the ethereal solution had been washed, the ether was removed by distillation, and an oily residue was left. This was mixed with the oily substance which had already been obtained, and the mixture was distilled. A large portion of the distillate proved to be unchanged *p*-cresol, but the fraction, which boiled at 240–255°, yielded on redistillation a syrupy liquid, which gave the characteristic reactions of homocatechol (3:4-dihydroxytoluene)—reduction of Fehling's solution and of ammoniacal silver nitrate in the cold, and with ferric chloride a green coloration which turned brown after some time. Homocatechol was the only oxidation product detected:



*Attempted Condensation of Resorcinol and of Quinol with Diethyl Ether.*—In view of the fact that diethylphenol was readily obtained by condensing phenol with ether with the aid of anhydrous aluminium chloride, we thought it desirable to attempt to prepare corresponding dihydric phenols by a similar direct method. Accordingly, a mixture of resorcinol with ether was treated with aluminium chloride in the manner described by Jannasch and Rathjen (*loc. cit.*). Only a slight reaction appeared to take place even when the mixture was heated, and when the product was

treated with water and worked up in the usual way, practically nothing but unchanged resorcinol was obtained. An attempt to condense quinol with ether was equally unsuccessful, and it is evident that these dihydric phenols do not undergo condensation with ether under the same conditions as lead to the formation of diethylphenol.

*Condensation of Phenol with Methyl Propyl Ether.*—In order to ascertain whether the reaction between phenol and diethyl ether could be extended to other ethers, we prepared some methyl propyl ether, and condensed it with phenol in the following manner. Thirty grams of phenol were dissolved in an equal weight of pure ether, the solution was cooled, and 120 grams of anhydrous aluminium chloride were slowly added in small portions. The mixture was then heated at  $140^{\circ}$  until no more hydrogen chloride was evolved, and, after cooling, the mass was decomposed with water and the oily product extracted with ether. The ethereal solution was washed and dried, the ether removed, and the residue distilled. A little unchanged phenol passed over first, but the bulk of the product distilled at  $130$ – $140^{\circ}$ . On redistillation of this fraction, an oily liquid, boiling at about  $135^{\circ}$ , was obtained. It is sparingly soluble in water, but easily so in alcohol or ether and in solutions of alkali hydroxides, and in aqueous solution it gives a dark green coloration with ferric chloride. Probably this compound is a *methylpropylphenol*,  $C_6H_5MePr\cdot OH$ . We propose to study the condensation of monohydric phenols with ethers more fully.

We take this opportunity of expressing our thanks to the Research Fund Committee of the Carnegie Trust for a grant which defrayed the expenses of this investigation.

CHEMISTRY DEPARTMENT,  
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CLVI.—*The Relation between Solubility and the Physical State of the Solvent in the Case of the Absorption of Carbon Dioxide in p-Azoxyphenetole.*

By IDA FRANCES HOMFRAY, D.Sc.

THERE appears to be, at the present time, a considerable amount of evidence to show that solution is, in general, a property of the amorphous, as distinguished from the crystalline, form of matter. As, however, this evidence is somewhat scattered, it is perhaps not undesirable to collate some of the more salient points.



A solution, in its widest sense, may be taken to mean a homogeneous phase of two or more components in variable proportions; it may be present in the gaseous, liquid, or solid state.

Solutions in the normal liquid phase can exist in equilibrium with almost all solids, liquids, and gases, and the same may be said of the gaseous phase, for the vapours of liquids and solids are all completely miscible.

When, however, we consider mixtures in the solid phase, we find that a definite distinction must be drawn between the amorphous and the crystalline forms.

The presence of directive forces and the formation of crystal faces appear almost entirely to prevent molecular interpenetration, mixtures of variable proportions being practically confined to isomorphous substances.

Thus, a finely divided crystalline precipitate is generally pure and easily freed from solution and moisture, whereas an amorphous precipitate always carries down with it both liquid and solid impurities in a state of intimate mixture indistinguishable from true solution, and, after drying, reabsorbs moisture from the air.

As has been pointed out by Roozeboom and others, no logical distinction can be drawn between the liquid and solid states, unless the latter term is restricted to the crystalline condition. Glass, a typically amorphous substance, can pass by gradual transition from the mobile liquid form, through all stages of viscosity, to a condition of mechanical rigidity, no triple point occurring in the system, which consists throughout of two phases only: vapour (negligible in this case) and congealing fluid. In this condition it must therefore be considered as a highly supercooled fluid. Like other fluids, it is capable of dissolving foreign substances, notably the metallic oxides used as colouring matter.

If, however, crystallisation sets in, it proceeds continuously without external agency to completeness, the supercooled state being a metastable one, and at the same time dissolved matter is separated from the crystals. The results are seen in some ancient stained glass windows, where devitrification is slowly, but irremediably proceeding.

The same distinction is very well exemplified by many of the igneous rocks, crystals of pure minerals being surrounded by an isotropic glassy matrix of homogeneous structure, but consisting of a solution of indefinite composition in the supercooled fluid state.

The gradual penetration of crystalline metals by gold appears at first sight to indicate solution in the crystalline state. The experiments have, however, been conducted under very high pressure, and both Ewing and Spring have shown that something

approaching liquefaction occurs on the surface of metals exposed to frictional pressure; the same probably takes place throughout the metal when under great stress, progressive solution of other metals accompanying it and producing uniform distribution.

The equilibria between gases and solids present many interesting points, but have not received much attention, except in the case of the absorption of hydrogen by palladium and platinum. It appears still uncertain whether this is a case of true solution or of an unstable chemical compound, the absorption being entirely selective, and taking place only at high temperatures.

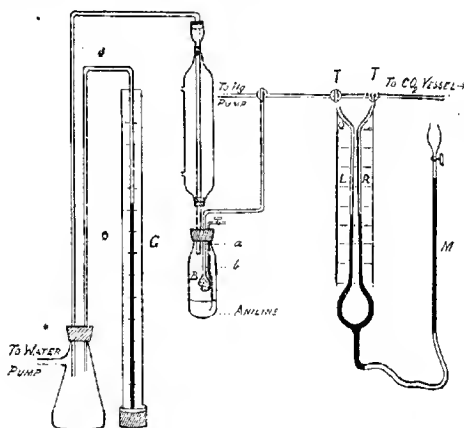
It has long been known that fused silver dissolves considerable quantities of oxygen, retaining it while in the supercooled state. On crystallising, the gas is evolved with considerable violence. Quite recently this phenomenon has been qualitatively investigated, together with the explosive crystallisation of antimony, due to the same cause (Sieverts, *Zeit. physikal. Chem.*, 1909, 68, 115). A curious case of the formation of air bubbles expelled from solution on the devitrification of glass slag has, I believe, been brought to the notice of geologists on the north-west coast of England, where the floating glass was washed up and at first mistaken for the product of submarine volcanic action. At low temperatures, amorphous nickel oxide can dissolve considerable quantities of gas, and the quantitative study of the laws governing the equilibria between charcoal and various gases has led the author (*Proc. Roy. Soc.*, 1910, A, 84, 99) to the conclusion that the absorption is to be attributed rather to solution in the highly supercooled fluid than to surface condensation. Also, on heating the charcoal to a high temperature, its absorptive power is permanently much reduced, probably owing to partial crystallisation, for, on converting it completely into graphite, the property is entirely lost.

In view of the foregoing considerations, it is obviously of considerable interest to investigate the solubility of gases in substances which can exist, between definite temperature limits, in the rigid crystalline, liquid crystalline, and isotropic liquid forms. For, according to this view, the two first phases must both be classed as solids, and may be expected to have considerably smaller solvent power than the isotropic liquid. It has been shown by Schenck (*Zeit. physikal. Chem.*, 1898, 25, 337) that isotropic liquids are not miscible with the crystalline liquid phase; the present investigation is therefore confined to the question of the solubility of gases, carbon dioxide being the most suitable.

These phases are produced at successively higher temperatures, and if, therefore, either or both changes of phase is accompanied

by a considerable increase of gas absorption, the temperature-pressure diagram should show definite maxima and minima. It appears from the researches of Lehmann, and more recently of Vorländer, Hulett, Schenck, and others, that there is little reason to doubt the truly crystalline structure of the anisotropic liquid.

The first experiments to be described were carried out with *p*-azoxyphenetole (obtained direct from Kahlbaum and recrystallised), and, in spite of the comparatively high melting and clearing points ( $156.5^{\circ}$  and  $161.7^{\circ}$ ), and consequent very small actual volume of gas dissolved, well marked maxima and minima were consistently recorded in the numerous series of measurements under slightly modified conditions which were required before



quantitative results were obtained. It was, of course, also necessary to prove conclusively that no chemical action takes place, even at the highest temperatures required.

The apparatus used is shown in the accompanying diagram.

The differential manometer *L, R*, as well as the connecting tubes to the experimental bulb *B* and the gas-holder, were of thick-walled glass tubing of 2 mm. bore. The two manometer taps *T, T* were of the pattern containing a T-shaped bore, so that the whole apparatus could be evacuated with the mercury pump or the pressure equalised throughout with that in the gas holder.

The required temperatures were obtained by immersing the bulb and a definite length of the tubing *ba* in a large test-tube containing aniline boiling under diminished pressure. By means of

the water-pump and a spring pressure-regulator, it was found that the pressure could be kept constant to within a few millimetres. The readings of the single-tube gauge *G* give differences from observed barometric height, whence the temperatures are obtained from the known vapour-pressure curve for aniline. After evacuation, pure dry carbon dioxide was admitted from the gas-holder, all taps being open, and the levels in the two limbs *L* and *R* of the manometer consequently the same.

The taps *T, T'* were then turned so that the limb *R* connected only with the gas holder, and the limb *L* only with the experimental bulb. The mass of gas in the bulb *B*, tubes *ba* and *aO*, and limb *L*, to the mercury level, is therefore constant, whilst the pressure in the limb *R* is the same as that in the gas holder, and is found by reading, on the scale, the difference of level between the mercury in *R* and in the open tube *M*. By having a large mercury reservoir, this pressure is not sensibly affected by changes in atmospheric temperature. As a rule, the reservoir was fixed so that the excess pressure over the atmospheric was about 15 cm. of mercury.

The calibration of the apparatus was effected by removing the aniline jacket and immersing the bulb and tube *ba* in melting ice, water at 19°, and the vapours of boiling alcohol and boiling water successively. The mercury in the left limb of the manometer was adjusted to certain definite points of the scale between 0 and 40 cm., and the difference of height in the two limbs was read. The difference of pressure with change of volume was thus determined, the temperature of the exposed tubes and manometer being kept constant throughout at 19°.

From three such determinations, it is possible to calculate the volume of gas in the bulb and tube *ba*, and in the connecting tubes *aO* at 19° and 76 cm. pressure, and also the total volume of gas in the apparatus in terms of the volume of 1 cm. length of the manometer scale. The numbers obtained were:

Bulb and immersed tube .....	262.6 cm.	<i>x</i>
Connexions to zero point (0).....	82.6 "	<i>y</i>
Total volume ... ..	364.0 "	<i>M</i>
Volume of 1 cm. of tube (by calibration) ...	0.029 c.c.	

The general formula used in calculation is:

$$x \frac{293}{P} + y + N = M \frac{76}{P},$$

where *N* is the required number of scale divisions.

The difference of the other observed readings from those calculated from the above data did not exceed 2 or 3 millimetres, showing that the manometer was of sufficiently even bore, also that no gas

was evolved from the crystals on heating to  $100^{\circ}$ , and that no reaction had occurred.

The aniline vapour-bath was then replaced, and the temperature raised to successively higher temperatures.

In the succeeding absorption measurements, the mercury was always brought to the same level in the two tubes by raising or lowering the reservoir *M*, change of volume at constant pressure being thus measured, and the necessarily very small effects greatly magnified. The numbers so obtained therefore correspond with changes in volume of the gas in the heated portion of the apparatus due to thermal expansion and change of solubility, in terms of the volume of gas in unit length of the manometer scale, at constant known temperature and pressure. A thermometer suspended near the manometer stand enabled a small correction to be applied for changes in the laboratory temperature. The differences between the observed and calculated numbers, at various temperatures, then give the volumes of gas absorbed, in the same units.

Up to a temperature just below the first melting point, the readings agreed almost exactly with the volumes calculated for the successive temperatures. It is thus proved that, even with the very sensitive method employed, no change of gas absorption is observable between the temperatures of  $0^{\circ}$  and  $131^{\circ}$ . It seems impossible that, if any appreciable condensation of gas on the surface of the crystals occurs at low temperature, the same should persist over a wide range of temperature. It may therefore be taken as demonstrated that neither adsorption nor solution in the solid phase occurred, although the crystals consisted of small, very thin plates, uniformly well shaped, and recovering their original form completely after having been melted.

After the first melting point, absorption takes place, the observed volume diminishing considerably until equilibrium is reached. On further raising the temperature, normal thermal expansion again occurs, a minimum reading having thus been passed through. Expansion continues until the clearing point is reached. As soon as the isotropic liquid phase is reached, a second very well marked increase of absorption is observed, equilibrium being again reached at constant temperature. After this, expansion and decrease of solubility with rise of temperature proceed regularly.

On reversing the process by causing the aniline in the vapour jacket to boil at successively lower pressures, the corresponding maximum and minimum readings are repeated, although there is, of course, generally a considerable lag due to the very slow evolution of gas in passing from the isotropic to the liquid

crystalline phase. The identical readings may, however, often be recovered, with sufficient patience, on the return journey. The following table gives a typical experiment:

P.	t°.	Number of divisions.		D.
		Observed.	Calculated.	
92.4	100	10.0	10.0	0.0
92.4	131	24.3	24.2	0.1
90.6	143	38.6	39.4	0.8
—	158	16.6 (crystalline liquid)	45.0	28.8
—	160	17.1	45.9	28.8
—	161	13.0 (isotropic)	46.2	33.2

It was found, on comparing the melting and transition temperatures observed with those given by other experimenters, that the first melting point was too high, whilst the transition point was too low, the same numbers being obtained in the absence of carbon dioxide. It was therefore necessary to prepare and purify a fresh sample, that first used being presumably impure.

*p*-Nitrophenetole was recrystallised repeatedly from absolute alcohol, and then heated with sodium in absolute alcoholic solution. It was found that the best yields were obtained by boiling for only about a quarter of an hour with a reflux condenser, longer heating only increasing the amount of dark-coloured aldehydic resin. After cooling, the alcohol was decanted and the residue recrystallised some twenty times from absolute alcohol. The azoxy-compound is then obtained in fine, crystalline, pale yellow plates. The final yield is, however, small. The correct melting points, 138.5° and 168°, were then obtained. Two grams were taken, and the absorption experiments were carried out as before. The former results were completely confirmed, but, owing to the extension of the crystalline liquid phase, more readings could be obtained.

The following table gives the results of one series of measurements.

The equation from which the calculated values *N* were obtained was:

$$239.4 \times \frac{293}{T} + 77 + N = 280.4.$$

The constant pressure was 88.5 cm.

t°.	State.	N observed.	N calculated.	Difference.
134.0	(solid)	31.0	31.0	0
139.5		34.8	33.4	-1.4
145.5	(crystalline liquid)	17.7	35.8	18.1
149.0		19.6	37.2	17.6
156.5	"	22.5	40.1	17.6
160.0	"	23.0	41.4	18.4
164.5	"	24.2	43.0	18.8
166.5	"	24.3	43.8	19.5
168.5	(liquid)	17.4	43.8	26.4
167.5	"	18.0	44.2	26.2
169.0	"	18.6	44.7	26.1

# 1676. SOLUBILITY AND THE PHYSICAL STATE OF THE SOLVENT, ETC.

It is not to be expected that the liquid crystalline state would show the same impenetrability to gases as the rigid crystals, and we accordingly find considerable absorption in that phase. Also, it seems very probable that a certain amount of isotropic mother liquor may be present throughout the range of temperature in which the phase persists. This should not occur in the pure state, as the triple point is determined by a single temperature; the effect is probably due to the presence of the second component, namely, carbon dioxide, in solution. The melting point is decidedly less sharp than when dissolved gas is absent, and the temperature required is several degrees higher. Hulett (*Zeit. physikal. Chem.*, 1899, 28, 639) has shown by means of transition-point curves that, whereas all crystalline liquids are completely miscible, other substances, whether of higher or lower melting points, are immiscible in this phase, and may even prevent its formation.

In connexion with experiments on surface-tensions of the two phases, Schenck has determined the density curve of this and other similar substances, and it appears that in the case of *p*-azoxyphenetole, there is decided expansion on passing to the isotropic phase. It is therefore necessary to determine how far this fact may account for the increase of absorption. The volumes of 2 grams were calculated from the densities at two temperatures, respectively above and below the transition point. The results are given below, together with the actual volumes of gas absorbed in 100 c.c. of liquid, taking the volume of each centimetre of the manometer tube as 0.03 c.c.:

$t^{\circ}$ .	N absorbed.	Volume. absorbed.	Volume of liquid.	Absorbed in 100 c.c.
145.5	18.1	0.54	1.824	29.6 c.c.
166.5	26.4	0.79	1.866	42.3 „

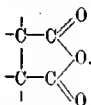
It is thus evident that the correction introduced is quite inappreciable on the scale of the present measurements, and the remarkable increase of absorption on changing from the crystalline to the isotropic phase, occurring in spite of the considerable rise of temperature, can only be attributed to the influence of the physical state of the solvent.

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CLVII.—*The Rate of Hydration of Acid Anhydrides: Succinic, Methylsuccinic, Itaconic, Maleic, Citraconic, and Phthalic.*

By ALBERT CHERBURY DAVID RIVETT and NEVIL VINCENT SIDGWICK.

THE present communication is an extension of the work on the rate of hydration of acetic anhydride (this vol., p. 732) to a series of anhydrides all containing the five-atom ring:



The method adopted was, as before, to measure at appropriate intervals of time the electrical conductivity of a changing solution of the anhydride in water, and to determine, over the same range of concentrations, the conductivity of aqueous solutions of the corresponding acid. As was pointed out (*loc. cit.*), the only condition in which the former measurements differ from the latter is in the presence of the unchanged anhydride, which may affect the conductivity by its influence on the viscosity, but will presumably have no other effect. In the only three cases where this condition need be considered, we have assumed that the conductivity is inversely proportional to the viscosity, and further, as was proved to be the case with acetic anhydride, that the viscosity of a solution of the anhydride is equal to that of an equivalent solution of the corresponding acid. Even if this is only approximately true, the error in the correction introduced will be slight.

In every instance we have redetermined the conductivities of the acids dealt with, because the accuracy of the velocity figures is greatly increased by making these measurements under as nearly as possible the same conditions as those obtaining in the velocity experiments. The same cells were therefore used for both purposes. The accuracy of the conductivity measurements is in all cases rather greater than is actually needed. The method adopted, of successive dilutions in the cell (every second dilution being checked by weight titration against 0.1 or 0.02*N*-baryta), is not the one which would be chosen for the highest accuracy, especially at the dilute end of a series. It is, however, unlikely that the error of measurement is anywhere greater than 1 part in 300, except perhaps in some of the most dilute solutions.



The slight modifications in the method of working necessary in particular cases will be mentioned under the respective anhydrides. Unless otherwise stated, the substances were obtained from Kahlbaum.

#### EXPERIMENTAL.

##### 1. Succinic Anhydride.

The acid was purified by twice recrystallising from water, the anhydride by extraction with chloroform in a Soxhlet apparatus, and crystallisation from this solvent. It separates in long needles, melting at  $119.5^{\circ}$  (uncorr.). The cell used was about 160 c.c. in volume, with the electrodes sealed in; 120 c.c. of solution were always used. In the case of acetic anhydride, which is liquid, solution is so rapid that the time of mixing could be taken as the zero of the reaction, and the solution, after a brief period of shaking, could be poured into the cell, and the measurements begun. Succinic anhydride, being solid, dissolves much more slowly, and the following modification was necessary. A known weight of the anhydride was added to the right volume of water in a Jena flask (heated in the bath to  $25^{\circ}$ ), and the stop-watch started. The mixture was violently shaken in the bath for from thirty-five to sixty seconds, and then rapidly drawn over by suction into the cell, passing on its way through a thick and closely packed filter of glass wool to retain undissolved particles. After shaking round in the cell, measurements were begun. The end-point was usually taken about two hours later. For the calculation it was necessary to take an initial time more definite than the beginning of solution. The first six or eight measurements were therefore plotted against the time, and a value of the concentration and time to be used as the starting point, and to be subtracted from all subsequent values, was obtained by interpolation. This time was usually about 140 seconds from the addition of the anhydride. The velocity constant is apparently quite independent both of the concentration of the anhydride and also of that of the acid, so that the calculation can be begun at any point.

As with acetic anhydride, the hydration follows the unimolecular law, that is, the rate is proportional to the concentration of the anhydride, that of the water being relatively constant at the dilutions used. But whereas with acetic anhydride a distinct though small variation of the constant with concentration was found to occur, no such variation was observed with succinic, nor with any of the cyclic anhydrides examined, with the possible exception of succinic.

$I_a$  gives the specific conductivity of solutions of succinic at  $25^{\circ}$ ;  $I_d$  the densities and viscosities, referred to water at

5° as unity. It gives the full details of a typical velocity experiment, and in the summary of all the experiments performed. In the last two tables,  $A$  is the difference between the concentration of the acid after the change is complete and that at time 0; it thus represents the concentration of the anhydride (in equivalent normality) at time 0;  $t$  is the time in seconds, and  $x$  the concentration of acid produced in time  $t$ .  $k$  is calculated from the equation:

$$k = 1/t \log \frac{A}{A-x}$$

TABLE I.

## (a) Conductivity of Succinic Acid Solutions at 25°.

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0.9813	1.955	0.06735	0.5534
0.8172	1.820	0.05622	0.5045
0.6806	1.687	0.04694	0.4537
0.5676	1.558	0.03911	0.4188
0.4730	1.438	0.03260	0.3869
0.3944	1.321	0.02721	0.3467
0.3285	1.214	0.02267	0.3156
0.2737	1.113	0.01987	0.2946
0.2279	1.019	0.01890	0.2869
0.2006	0.9580	0.01657	0.2682
0.1899	0.9320	0.01381	0.2435
0.1673	0.8756	0.009603	0.2007
0.1394	0.8006	0.006697	0.1656
0.1162	0.7298	0.004676	0.1384
0.09696	0.6661	0.003267	0.1120
0.08083	0.6077	0.002281	0.0918

## (b) Density and Viscosity of Succinic Acid Solutions at 25°.

Normality.	Density.	Normality.	Viscosity.
0.9805	1.0165	0.9305	1.1102
0.8235	1.0093	0.6979	1.0815
0.2214	1.0040	0.2351	1.0344
0.09869	1.0017	0.1248	1.0144
0.03950	1.0007		

(c) Experiment 8.  $A = 0.1665$ .

$t$ .	$x$ .	$k$ .	$t$ .	$x$ .	$k$ .
8	0.00343	0.001153	257	0.0823	0.001152
29	0.01218	1139	279	0.0870	1151
37	0.01531	1139	317	0.0949	1156
59	0.02414	1156	342	0.1001	1167
80	0.03134	1134	373	0.1051	1162
90	0.03514	1146	419	0.1121	1159
104	0.03966	1137	462	0.1184	1167
131	0.0489	1153	523	0.1253	1160
145	0.0532	1153	589	0.1326	1174
161	0.0578	1150	676	0.1390	1157
181	0.0636	1155	971	0.1543	1169
213	0.0721	1157	1185	0.1593	1151
235	0.0771	1149		Mean.....	0.001154

*(d) Summary of Velocity Experiments.*

Expt.	A.	k.	Expt.	A.	k.
1	0.01113	0.001148	8	0.1665	0.001154
2	0.02042	1156	9	0.1873	1162
3	0.03220	1151	10	0.2746	1146
4	0.05261	1148	11	0.3145	1168
5	0.08093	1156	12*	0.1580	1165
6	0.10833	1152			
7.	0.1373	1155		Mean .....	0.001155

\* In this experiment, the anhydride was dissolved in water already containing acid of normality 0.3805.

*2. Methylsuccinic Anhydride.*

This anhydride was prepared from a pure sample of the acid by the method described by Perkin (Trans., 1888, **53**, 564). It consists in digesting the acid with acetyl chloride until action ceases, and fractionally distilling the product. The anhydride passed over within one degree, and was readily purified by redistillation. Like citraconic anhydride, it has a slight yellow colour after being distilled. It gave no trace of a precipitate with silver nitrate. The method of working was the same as with acetic anhydride. The cell had a volume of 100 c.c., and 80 c.c. of solution were always taken. The results are given in table II, in the same form as those for succinic anhydride in table I.

TABLE II.

*(a) Conductivity of Methylsuccinic Acid Solutions at 25°.*

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0.4309	1.540	0.04425	0.4991
0.3233	1.352	0.03356	0.4304
0.2427	1.183	0.02539	0.3708
0.1821	1.029	0.01940	0.3189
0.1367	0.8935	0.01455	0.2738
0.1026	0.7745	0.01092	0.2352
0.07702	0.6702	0.00819	0.2015
0.05782	0.5787	0.00614	0.1726

*(b) Density and Viscosity.*

Normality.	Density.	Viscosity.
0.4885	1.0079	1.076
0.3456	1.0056	1.032
0.1638	1.0026	1.024

## (c) Summary of Velocity Experiments.

Expt.	A.	k.	Expt.	A.	k.
13	0.03624	0.001653	18	0.1449	0.001599
14	0.05779	1666	19	0.1778	1570
15	0.05973	1636	20	0.2330	1580
16	0.09953	1602	21	0.2755	1573
17	0.1210	1597	Mean	.....	0.001609

## 3. Itaconic Anhydride.

The acid and its anhydride were purified in the same way as succinic. Itaconic anhydride forms crystals which dissolve very rapidly in water. The stronger solutions were made in the way described under succinic anhydride, and the more dilute by simply placing an approximately known weight of the solid on a firm glass wool filter, and sucking the required amount of water through it directly into the cell. The initial point for the calculation was obtained by interpolation. The results are given in table III.

TABLE III.

## (a) Conductivity of Itaconic Acid at 25°.

Normality.	Specific conductivity × 1000.
0.3870	1.946
0.2904	1.705
0.2179	1.487
0.1636	1.292
0.1227	1.120
0.09208	0.9686
0.06911	0.8366
0.05180	0.7208
0.03925	0.6207
0.02963	0.5338
0.02259	0.4537
0.01720	0.3934
0.01294	0.3375
0.009726	0.2883
0.007326	0.2462
0.005515	0.2099
0.004136	0.1785

## (b) Density and Viscosity.

Normality.	Density.	Viscosity.
0.3433	1.0064	1.049
0.2689	1.0050	1.038
0.1484	1.0023	1.022

## (c) Summary of Velocity Constants.

Expt.	A.	k.
23	0.01561	0.001283
24	0.02034	1320
25	0.02561	1305
26	0.04689	1238
27	0.07135	1273
28	0.07955	1264
29	0.09587	1303
30	0.1371	1311
31	0.1793	1311
32	0.2269	1283
Mean	.....	0.001294

## 4. Maleic Anhydride.

The anhydride was purified by sublimation in a vacuum, and the acid solutions required were made up directly from this. The substance dissolves fairly rapidly, but is very quickly hydrated; as a rule, the change was found to be practically complete about two and a-half minutes after the making of the solution was begun. Hence the measurements must be made as quickly as possible, and the accuracy is reduced.

The solutions were all obtained by sucking water into the cell over a layer of anhydride on a glass wool filter. It was, of course, impossible to obtain strong solutions, and no correction for viscosity was necessary. An approximate initial time was taken when half the water had been drawn into the cell, but for the calculation: zero time, usually about forty seconds later than this, was arrived at by interpolation. The results are given in table IV.

TABLE IV.

## (a) Conductivity of Maleic Acid.

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0.06031	5.503	0.009385	1.368
0.04525	4.515	0.007055	1.075
0.03930	4.098	0.005334	0.896
0.03394	3.087	0.004021	0.6521
0.02949	3.330	0.003042	0.5032
0.02213	2.095	0.002304	0.3865
0.01664	2.186	0.001728	0.2954
0.01250	1.724	0.001296	0.2252

(b) Experiment 37.  $A=0.00353$ .

$t$ .	$x$ .	$k$ .	$t$ .	$x$ .	$k$ .
0	0.00054	0.0120	57	0.00277	0.0117
9	0.00082	116	66	0.00298	117
14	0.00105	110	70	0.00307	116
18	0.00133	114	87	0.00317	114
23	0.00160	114	99	0.00326	113
28	0.00189	119	114	0.00334	111
35	0.00217	118	153	0.00347	116
42	0.00235	113			
49	0.00259	117			
			Mean .....	0.0115	

## (c) Summary of Velocity Constants.

Expt.	$A$ .	$k$ .	Expt.	$A$ .	$k$ .
33	0.000985	0.0114	33	0.00049	0.0108
34	0.001771	122	39	0.01094	110
35	0.001537	113	40	0.01961	118
36	0.002999	119			
37	0.00353	115	Mean .....	0.0115	

## 5. Citraconic Anhydride.

The anhydride was purified by distillation. It has a slight yellow colour. The acid solutions were made up from this. The method of work was the same as with acetic and methylsuccinic anhydrides. The range of concentration employed was much the same as with maleic anhydride, and no correction for viscosity was necessary. The results are given in table V.

TABLE V.

## (a) Conductivity of Citraconic Acid.

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0.10268	4.476	0.01376	1.275
0.07683	3.787	0.01034	1.045
0.06763	3.189	0.007775	0.8506
0.04326	2.679	0.005818	0.6882
0.03245	2.240	0.004358	0.5527
0.02436	1.868	0.003260	0.4405
0.01633	1.547	0.002452	0.3485

## (b) Summary of Velocities.

Expt.	A.	k.	Expt.	A.	k.
41	0.004305	0.00761	47	0.05005	0.00761
42	0.006634	771	48	0.06100	776
43	0.01407	769	49	0.07504	758
44	0.02074	777	50	0.08287	761
45	0.06093	758			
46	0.03622	761			
				Mean .....	0.00765

## 6. Phthalic Anhydride.

The acid was recrystallised twice from water, and the anhydride twice from xylene. The method of working, and of determining the initial point for the calculation, was that adopted for succinic anhydride, but owing to the small solubility of both acid and anhydride, the concentrations examined are all low, although the relative range is considerable. No viscosity correction is necessary. Table VI gives the results obtained.

TABLE VI.

## (a) Conductivity of Phthalic Acid at 25°.

Normality.	Specific conductivity × 1000.	Normality.	Specific conductivity × 1000.
0.05506	1.354	0.008946	0.6856
0.04587	1.763	0.007474	0.5917
0.03819	1.592	0.006228	0.5268
0.03181	1.437	0.004955	0.4427
0.02652	1.293	0.004149	0.3913
0.02210	1.159	0.003486	0.3460
0.01843	1.042	0.002427	0.2651
0.01539	0.934	0.001686	0.2037
0.01283	0.8358	0.001188	0.1530
0.01071	0.7469	0.000825	0.1145

## (b) Summary of Velocities.

Expt.	A.	k.	Expt.	A.	k.
51	0.000650	0.00470	56	0.002145	0.00455
52	0.001043	470	57	0.00348	454
53	0.001320	466	58*	0.00382	454
54	0.001855	469			
55	0.002120	466			
			Mean .....	0.00461	

\* In this experiment, the anhydride was dissolved in water already containing acid of normality 0.02754.

## Discussion of Results.

The mean velocity constants for the hydration of this series of anhydrides are given in the following table, together with the dissociation constants of the corresponding acids.

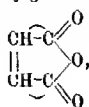
Anhydride.	Velocity constant.		Dissociation constant of acid.	
	Absolute.	Relative.	Absolute.	Relative.
[Acetic .....	0.001148	0.99]	—	—
Succinic.....	0.001155	1.00	0.0068	1.00
Methylsuccinic.....	0.001609	1.39	0.0068	1.30
Itaconic (methylenesuccinic)	0.001294	1.12	0.012	1.82
Maleic .....	0.0115	9.96	1.2	182.0
Citraconic (methylmaleic) ...	0.00765	6.62	0.34	51.5
Phthalic .....	0.00461	3.99	0.121	18.3

The mean value for acetic anhydride, over the range of concentrations covered by the succinic experiments, has been added for comparison; the individual values vary from 0.001192 to 0.001075.

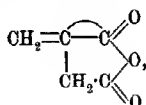
It is to be noticed, in the first place, that in none of the cases examined is there any evidence of a catalytic influence of hydrogen-ion; and it seems clear that the mechanism of the hydration of an acid anhydride is quite different from that of the hydrolysis of an ester or an amide.

Further, it is remarkable that in the cyclic anhydrides no dependence of the velocity constant on the concentration, such as was observed in acetic anhydride, was detected, except possibly in methylsuccinic anhydride, although even here the effect was very slight.

The close agreement between the constants for acetic and succinic anhydrides affords a good illustration of Baeyer's strain theory: the ring of four carbon atoms and one oxygen having practically no strain, and resembling most nearly an open-chain compound. In maleic anhydride, where there is a full double link, and indeed, according to Thiele, two conjugate links as well,



the constant is increased ten times; in phthalic there is the peculiar benzene link, which, whatever may be its precise nature, is intermediate in character between a single and a double link, and this increases the constant four times. In itaconic there is, on Thiele's theory, a conjugate link in the ring,



and this causes a slight rise in the constant.

The influence of a methyl group, however, is quite anomalous. Its introduction lowers the constant of maleic anhydride by a third, while it raises that of succinic by about two-fifths. It is noteworthy that the effect of the methyl on the dissociation constants of the corresponding acids is likewise in the opposite direction in these two cases; in fact, in general the order of the dissociation constants of these acids is the same as that of the hydration constants of their anhydrides, except in the case of methylsuccinic and itaconic, where, moreover, the differences are not large. It is evident that with these substances the same changes of structure, and especially the introduction of double links, tend to increase both of these constants, though how far this regularity may be general, and how far stereochemical influences (which would presumably affect the hydration rather than the ionisation, and may possibly account for the exceptional position of methylsuccinic anhydride) may come into play, is a question which cannot be discussed until a wider range of anhydrides has been examined.

The considerable diminution of the hydration constant of maleic anhydride caused by the introduction of a methyl group is of interest in view of the singular behaviour of dimethylmaleic anhydride. This anhydride is formed spontaneously from the acid, which, in fact, cannot be isolated. It has been shown by Walden (*Zeitsch. physikal. Chem.*, 1891, 8, 498) that an aqueous solution of dimethylmaleic anhydride (and similarly of methylethylmaleic anhydride) can only contain a comparatively small amount of the corresponding acid, since conductivity measurements indicate an abnormally low dissociation constant, and the solution can only be slowly titrated with alkali. The arguments by which Walden seeks to prove that the rest is not present as anhydride are of no great force, and we may assume that with these two substances the hydration is reversible, and that at equilibrium there is present a large proportion of anhydride and a small proportion of acid. It is conceivable that the reaction may also be reversible with some



of the substances which we have examined. We did not observe in any case a difficulty in the titrations, but this might well be imperceptible if the amount of anhydride were small. If the reverse action (acid  $\rightarrow$  anhydride) is also unimolecular, and its velocity is  $k_1$  (that of the direct action being  $k$ ), it can easily be shown that the substance will give an apparent dissociation constant independent of the dilution, but that this will be less than the real dissociation constant in the ratio  $1 : (1 + k_1/k)$ . In the same way, the apparent hydration constant will also be independent of the dilution, but instead of being, as we have assumed, the true hydration constant  $k$ , will be the sum of the two,  $k + k_1$ . Thus, the effect of the reverse action being appreciable would be to make the apparent value of the dissociation constant too low (as it does with dimethylmaleic anhydride), and that of the hydration constant too high. It therefore could not possibly explain the anomalous effect of the methyl group, which influences both constants in the same way. In any case, the amount of the reverse action with the bodies which we have examined must be small, or it would have shown itself in the absence of a sharp end-point to the titrations.

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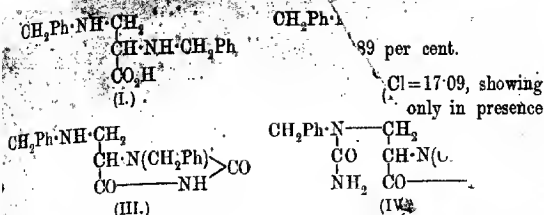
#### CLVIII.— $\alpha\beta$ -Dibenzylaminopropionic Acid and 1:7-Dibenzyltetrahydrouic Acid.

By EDWARD PERCY FRANKLAND.

THE present paper describes the synthesis of 1:7-dibenzyltetrahydrouic acid (IV) on the lines followed by the author in the recent synthesis of tetrahydrouic acid from  $\alpha\beta$ -diaminopropionic acid (this vol., p. 1316), namely, by the addition of cyanic acid to the substituted amino-groups, followed by condensation by means of hydrochloric acid.

The new dibenzyltetrahydrouic acid is of interest in view of the fact that Tafel, the discoverer of tetrahydrouic acid, was unable to produce substituted tetrahydrouic acids by the electrolytic reduction of the methyluric acids, and that consequently substances of this class appear to be accessible only from the synthetic side.

Starting from the hitherto unknown  $\alpha\beta$ -dibenzylaminopropionic acid (I), it was found possible to isolate several intermediate compounds before dibenzyltetrahydrouic acid (IV) was produced,



whereas in the case of the synthesis of tetrahydric acid  $\beta$  in  $\alpha\beta$ -diaminopropionic acid, no such analogous substances could be obtained, serving to illustrate the course of the reaction.

In the present case, the difference in chemical behaviour between the  $\alpha$ - and the  $\beta$ -benzylamino-groups is strikingly shown, only one group reacting with potassium cyanate even in presence of excess of the reagent. This fact suggests that one or other of the imino-groups is shielded either by steric obstruction or by combination with the free carboxyl group, forming an internal salt. Judging from the action of nitrous acid on the  $\alpha\beta$ -diamino-acid, in which case the  $\beta$ -group appears to be indifferent to the reagent, in the present instance it seems most likely that the cyanic acid attaches itself to the  $\alpha$  group. Thus, for the compounds described below, it has been decided to omit the alternative formulæ based on the primary addition of cyanic acid to the  $\beta$ -benzylamino-group. Further investigations are, however, being carried out with the view of testing the above hypothesis.

$\alpha\beta$ -Dibenzylaminopropionic acid was prepared by the action of benzylamine on  $\alpha\beta$ -dihromopropionic acid in chloroform solution; it is capable of uniting with two molecules of hydrochloric acid to form a salt. As was shown by Tafel and Frankland (*Ber.*, 1909, 42, 3138) in the case of  $\beta$ -amino- $\alpha$ -methylaminopropionic acid and  $\beta$ -dimethylaminopropionic acid dihydrochlorides, hydrogen chloride is readily eliminated in aqueous solution, probably with formation of an internal salt between one of the benzylamino-groups and the carboxyl.

When a hot aqueous solution of dibenzylaminopropionic acid was treated with potassium cyanate (2 molecules) and hydrochloric acid, it yielded  $\beta$ -benzylamino- $\alpha$ -benzylcarbamidopropionic acid (II), which, on warming with 25 per cent. hydrochloric acid, was converted into  $\beta$ -benzyl- $\gamma$ -benzylaminomethylhydantoin hydrochloride. The principal product of the action of potassium cyanate on this substance was the free  $\beta$ -benzyl- $\gamma$ -benzylaminomethylhydantoin (III), but by the long-continued action of potassium cyanate and hydrochloric acid in aqueous methyl alcohol, this compound could

of the substances which are derivatives, 1: 7-dibenzyltetrahydroure  
 in any case a difficulty in perceiving the  
 perceptible if the  
 reverse action (acid velocity is  $k_1$  (the  $\alpha\beta$ -Dibenzylaminopropionic Acid.

## EXPERIMENTAL

shown that the independent of  $\alpha\beta$ -dibromopropionic acid were dissolved in a  
 real dissof 14 grams of benzylamine in chloroform, and the mixture  
 way, heated to boiling under reflux. After about fifteen minutes,  
 the distillate precipitate was deposited, which, after being collected,  
 washed with chloroform, and dried, weighed 4.6 grams. This sub-  
 stance proved to be benzylamine hydrobromide (m. p.  $215^\circ$  after  
 recrystallisation from water). The reaction mixture was heated on  
 the water-bath until no further precipitation occurred; the chloro-  
 form was then distilled off, and the brown, oily residue heated in  
 the water-bath for half an hour longer. It was then extracted  
 with ether, and the residue dissolved in a mixture of boiling ethyl  
 and methyl alcohol; the solution was concentrated and precipitated  
 with ether. The precipitate of dibenzylaminopropionic acid was  
 washed with alcohol and ether, recrystallised from boiling water,  
 washed again with alcohol and ether, and, after drying in the  
 steam-oven, weighed 3.2 grams. By concentrating the mother  
 liquors (which contained a quantity of benzylamine hydrobromide),  
 0.5 gram of crude dibenzylaminopropionic acid was obtained.

The substance dissolved fairly easily in boiling water, and  
 separated from the cooled solution in large, crystalline aggregates;  
 it was very sparingly soluble in cold water (1: 898 at  $14^\circ$ ), the  
 solution showing an alkaline reaction to litmus, readily soluble in  
 warm methyl alcohol, sparingly so in absolute ethyl alcohol, and  
 almost insoluble in ether. It formed rhomboidal plates from methyl  
 alcohol, melting and decomposing at  $181-184^\circ$ :

0.2978 gave 0.7791  $\text{CO}_2$  and 0.1920  $\text{H}_2\text{O}$ .  $\text{C}=71.35$ ;  $\text{H}=7.19$ .

0.1274 „ 11.4 c.c.  $\text{N}_2$  at  $18^\circ$  and 739.7 mm.  $\text{N}=10.05$ .

$\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2$  requires  $\text{C}=71.83$ ;  $\text{H}=7.04$ ;  $\text{N}=9.86$  per cent.

A portion of the dibenzylaminopropionic acid was dissolved in  
 warm aqueous hydrochloric acid. After concentration on the  
 water-bath the solution deposited, on cooling, a white, crystalline  
 substance, which was collected, washed with dilute hydrochloric  
 acid, alcohol, and ether, and was dried in a vacuum desiccator.  
 The substance decomposed with blackening and evolution of gas at  
 $181-184^\circ$ . It was soluble in water, the solution showing an acid reaction  
 to litmus, soluble in alcohol, and insoluble in ether. A hydro-  
 chloric acid estimation showed this compound to be  $\alpha\beta$ -dibenzyl-  
 aminopropionic acid dihydrochloride:

0.1987 gave 0.1595 AgCl. Cl=19.86.

$C_{17}H_{20}O_5N_2 \cdot 2HCl$  requires Cl=19.89 per cent.

A specimen recrystallised from water gave Cl=17.09, showing that solutions of the dihydrochloride are stable only in presence of an excess of hydrochloric acid.

#### 1:7-Dibenzyltetrahydrouric Acid.

Three grams of dibenzylaminopropionic acid were dissolved in hot water and treated with 2.4 grams of potassium cyanate. After cooling, 3.6 grams of concentrated hydrochloric acid were added to the solution, giving rise to a slight effervescence. The solution was then concentrated on the water-bath, and after some time a crystalline precipitate was slowly deposited in white flakes. It was collected, washed with water, then with a little absolute alcohol, and finally with ether. After drying in the steam-oven, it weighed 2.4 grams. It crystallises from alcohol in spherical aggregates of small prisms, melting and decomposing at 200–201°, which are very sparingly soluble in water, soluble in alcohol, and insoluble in ether:

0.0450 gave 54.79 c.c.  $CO_2$  at N.T.P. and 4.75 c.c.  $N_2$  at N.T.P.\*  
C=65.47; N=13.24.

0.0821 gave 9.5 c.c.  $N_2$  at 20° and 752.8 mm. N=13.11.

$C_{18}H_{21}O_5N_3$  requires C=66.05; N=12.84 per cent.\*

*β-Benzylamino-α-benzylcarbamidopropionic acid* (II) was also obtained by treating an aqueous solution of dibenzylaminopropionic acid dihydrochloride with potassium cyanate, but a less pure product was obtained, and the yield was considerably smaller than that furnished by the method described above. A solution of 2 grams of this compound in about 20 c.c. of 25 per cent. hydrochloric acid was heated on the water-bath, whereupon a crystalline precipitate separated out, which was collected, washed with concentrated hydrochloric acid, then with a little absolute alcohol, and finally with ether. After drying in the steam-oven, it weighed 1.95 grams. The mother liquor yielded a further quantity of the substance (0.15 gram).

*β-Benzyl-γ-benzylaminomethylhydantoin hydrochloride* crystallises in stellate groupings of prisms, melting without noticeable decomposition at 224°. It is sparingly soluble in water, the solution showing an acid reaction to litmus, more easily soluble in methyl than in ethyl alcohol, and insoluble in ether:

\* Carbon and nitrogen combustion in a vacuum.

1690 FRANKLAND:  $\alpha\beta$ -DIBENZYLAMINOPROPIONIC ACID

0.1331 gave 14.7 c.c.  $N_2$  at  $21^\circ$  and 742 mm.  $N=12.27$ .  
 0.2779 " 0.1166 AgCl.  $Cl=10.38$ .  
 $C_{18}H_{19}O_2N_3$ . HCl requires  $N=12.16$ ;  $Cl=10.27$  per cent.

1.5 Grams of this hydantoin hydrochloride were dissolved in aqueous methyl alcohol, and treated with a strong aqueous solution of 0.45 gram of potassium cyanate. An oily precipitate was deposited, which after some time set to a crystalline mass. This was collected, washed with alcohol and ether, and dried in the steam-oven. A further quantity was isolated from the mother liquor and washings, the total weight obtained being 1.33 grams. Melting point  $178-180^\circ$ .

The substance was boiled with a mixture of ethyl and methyl alcohol, when a part (0.3 gram) remained undissolved and melted and decomposed at  $195-196^\circ$ .

The solution, on concentration, yielded a crystalline substance (0.25 gram), which was collected and washed with alcohol and ether. After two recrystallisations from methyl alcohol and drying in a vacuum desiccator, it melted at  $112-115^\circ$ .

$\beta$ -Benzyl- $\gamma$ -benzylaminomethylhydantoin (III) forms long, needle-shaped crystals, sparingly soluble in water, but soluble in alcohol or ether. For analysis, it was recrystallised from ether to remove the last traces of a substance of high melting point:

0.1292 gave 15.9 c.c.  $N_2$  at  $20^\circ$  and 739.5 mm.  $N=13.69$ .  
 $C_{18}H_{19}O_2N_3$  requires  $N=13.59$  per cent.

Treatment with hydrochloric acid yielded the hydantoin hydrochloride described above.

In a second experiment 2.5 grams of the hydrochloride were treated with a warm solution of 0.4 gram of potassium hydroxide, whereby a colourless oil was deposited, solidifying on cooling. This was doubtless the free base described above. A mixture of ethyl and methyl alcohol was added, and the solution was heated until the precipitate had redissolved. A methyl-alcoholic solution of 0.7 gram of potassium cyanate was then added. On cooling, a precipitate of long needles appeared, which was evidently the unattacked hydantoin. The mixture was consequently warmed again, and a second portion of 0.7 gram of potassium cyanate added, followed by 1.9 grams of concentrated hydrochloric acid. On cooling, a gummy substance separated out, with a mass of fine, needle-shaped crystals. On heating the mixture, the crystals redissolved in the solution, which was poured off from the gum, and the latter extracted with ether. The ethereal extract was evaporated, and the residue returned to the mother liquor; the undissolved portion corresponded with the substance of high melting

obtained in the first experiment and melted and decomposed at 189–190°.

The process was repeated five times, 0.7 gram of potassium being added on each occasion, the solution boiled for a while, then cooled, and treated with 0.9–1.0 gram of concentrated chloric acid. The resulting precipitate was extracted with ether as above described, and the portions insoluble in ether were collected and tested separately. The melting points obtained varied from 173° to 179°. The total yield of substance insoluble in ether amounted to 1.8 grams.

This product was boiled with a large volume of methyl alcohol under a reflux condenser until all but a small residue had dissolved. The solution was then filtered hot and concentrated to a small bulk. A pure white substance crystallised out, which was collected, washed with ether, and dried in the steam-oven. It formed aggregates of small, prismatic crystals, melting at 177–178°, which were very sparingly soluble in water, sparingly soluble in methyl alcohol, and insoluble in ether.

The results of analysis agreed with the composition of the expected 1:7-dibenzyltetrahydrouric acid (IV):

0.0490 gave 58.96 c.c.  $\text{CO}_2$  at N.T.P. and 6.23 c.c.  $\text{N}_2$  at N.T.P.\*  
C = 64.71; N = 15.95.

0.0996 gave 14.3 c.c.  $\text{N}_2$  at 23° and 747 mm. N = 15.90.

$\text{C}_{19}\text{H}_{20}\text{O}_3\text{N}_4$  requires C = 64.77; N = 15.91 per cent.

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\* Carbon and nitrogen combustion in a vacuum.



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point obtained in the first experiment and melted and decomposed at 189—190°.

This process was repeated five times, 0.7 gram of potassium cyanate being added on each occasion, the solution boiled for a time, then cooled, and treated with 0.9—1.0 gram of concentrated hydrochloric acid. The resulting precipitate was extracted with ether as above described, and the portions insoluble in ether were collected and tested separately. The melting points obtained varied from 173° to 179°. The total yield of substance insoluble in ether amounted to 1.8 grams.

This product was boiled with a large volume of methyl alcohol under a reflux condenser until all but a small residue had dissolved. The solution was then filtered hot and concentrated to a small bulk. A pure white substance crystallised out, which was collected, washed with ether, and dried in the steam-oven. It formed aggregates of small, prismatic crystals, melting at 177—178°, which were very sparingly soluble in water, sparingly soluble in methyl alcohol, and insoluble in ether.

The results of analysis agreed with the composition of the expected 1:1-dibenzyltetrahydrouic acid (IV):

0.0490 gave 58.98 c.c. CO<sub>2</sub> at N.T.P. and 6.23 c.c. N<sub>2</sub> at N.T.P.\*  
C=64.71; N=15.95.

0.0996 gave 14.3 c.c. N<sub>2</sub> at 23° and 747 mm. N=15.90.  
C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>N<sub>4</sub> requires C=64.77; N=15.91 per cent.

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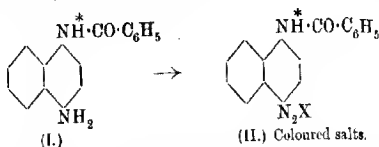
CLXXIX.—*The Colour and Constitution of Diazonium Salts. Part II. Diazo-derivatives of  $\alpha$ S-Benzoyl-ethyl-1:4-naphthylenediamine.*

By GILBERT T. MORGAN and EDWARD GORDON COUZENS, B.Sc.,  
A.R.C.S.

In a previous communication on diazonium salts it was shown that benzoyl-1:4-naphthylenediamine (I) gives rise to a series of remarkably stable diazonium derivatives (II), which are all dis-

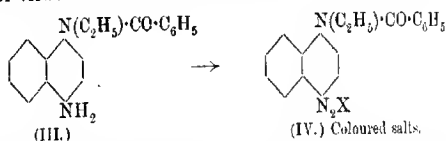
\* Carbon and nitrogen combustion in a vacuum.

tinctly coloured, usually in various shades of yellow (Morgan and Wootton, *Trans.*, 1907, **91**, 1311):



Inasmuch as colour and stability are not generally associated in diazonium salts (Hantzsch, *Ber.*, 1900, **33**, 2183; 1901, **34**, 4168), it was suggested that the concurrence of these properties in the diazo-derivatives of benzoyl-1:4-naphthylenediamine indicated a departure from the ordinary diazonium configuration. This view of the constitution of these salts is quite justifiable, because benzoyl-1:4-naphthylenediamine certainly contains one labile hydrogen atom (\*) which might migrate to the diazonium complex.

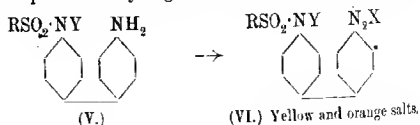
With the object of ascertaining whether this assumed migration of hydrogen is the cause of the stability and intense colour of benzoyl-4-aminonaphthalene-1-diazonium chloride and its analogues (II), the base *as-benzoyl-ethyl-1:4-naphthylenediamine* (III) and its diazonium salts (IV) were prepared and examined from this point of view:



These experiments showed that even when the labile hydrogen of benzoyl-1:4-naphthylenediamine is replaced by ethyl, the diazonium salts (IV) of the new base (III) are fairly stable, and retain their intense yellow colour even in dilute aqueous solution.

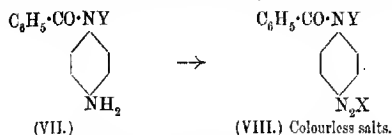
The observations recorded in the present communication should be compared with the evidence already obtained from a comparative study of similarly constituted salts in the diphenyl and benzene series.

In the former series, the bases having the general formula (V) give rise to stable coloured diazonium salts (VI), whether the symbol Y represents a hydrogen atom or an alkyl group:



A slight colour difference is noticeable in this series, the diazonium salts (VI), when Y is an alkyl group, being distinctly paler in tint than those in which Y is a hydrogen atom (Trans., 1907, **91**, 1505; 1908, **93**, 614).

In the latter series both benzoyl-*p*-phenylenediamine and its *o*-alkyl derivatives (VII) give rise to colourless diazonium salts (VIII) possessed of considerable stability (Trans., 1909, **95**, 1319):



In the benzene series, these diazonium salts are uniformly colourless, in the diphenyl series they are coloured to a varying extent, whilst in the naphthalene series the colour is approximately the same whether the salt is derived from benzoyl-1:4-naphthylene-diamine or its ethyl derivative.

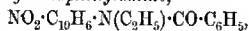
This comparative study of a series of fairly stable diazonium salts containing benzene, diphenyl, and naphthalene nuclei leads to the conclusion that the appearance of colour in this class of diazo-derivatives is due, not to any change in the constitution of the diazonium group, but to a gradual increase in the complexity of the aromatic nucleus associated with the diazonium radicle.

#### EXPERIMENTAL.

##### *o*-Benzoyl-ethyl-1:4-naphthylenediamine (III).

4-Chloro-*o*-nitronaphthalene (20 grams) was heated in a steel tube, closed with steel caps and leaden washers, for six hours with 80 c.c. of alcohol and 50 c.c. of 33 per cent. alcoholic ethylamine. The product, 4-nitroethyl-*o*-naphthylamine, was separated from unchanged chloro-compound by extraction with light petroleum, the yield being about 50 per cent.

*Benzoyl-4-nitroethyl- $\alpha$ -naphthylamine*,



prepared by heating 5 grams of the preceding compound in dry toluene with a slight excess of benzoyl chloride, crystallised from benzene or alcohol in pale yellow prisms, and melted at 121° (yield, 80 per cent):

0.2337 gave 18.3 c.c.  $\text{N}_2$  at 21° and 766 mm.  $\text{N} = 8.89$ .

$\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$  requires  $\text{N} = 8.75$  per cent.

The nitro-compound (4 grams) was dissolved in 50 c.c. of alcohol, and reduced with 3.5 grams of tin and 12 c.c. of concentrated



hydrochloric acid. After boiling for about thirty minutes, the cooled solution yielded a pink, crystalline precipitate, probably a stannichloride. This product, when decomposed with warm aqueous sodium hydroxide and extracted with benzene, furnished a base which, after recrystallisation from the same solvent, separated in small, yellowish-white needles, and melted at 205°:

0.2817 gave 23.8 c.c.  $N_2$  at 19° and 762 mm.  $N=9.74$ .

$C_{19}H_{18}ON_2$  requires  $N=9.65$  per cent.

*Benzoyl ethyl-4-aminonaphthalene-1-diazonium Sulphate.* — The foregoing base (0.5 gram) was suspended in 2 c.c. of glacial acetic acid, and treated with an equal weight of nitrosyl sulphate. A yellow coloration developed immediately and deepened rapidly, until after about thirty minutes a drop of the solution diluted with water no longer gave a precipitate of the unchanged base. In order to complete the diazotisation, it was sometimes found necessary to warm the acetic acid solution, but this procedure should be avoided so far as possible.

The solution of diazonium sulphate was then poured into six or seven times its volume of warm dry ether, when the diazonium salt was precipitated as a yellow oil, which solidified only after treatment with alcohol. Addition of more alcohol and ether to the supernatant mother liquor produced a further precipitation of crystalline diazonium salt, the total yield being practically quantitative. The following analyses were made on different specimens of the diazonium sulphate:

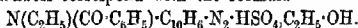
0.1330 gave 10.6 c.c.  $N_2$  at 15° and 765 mm.  $N=9.40$ .

0.2667 „ 22.3 c.c.  $N_2$  „ 19° „ 759 mm.  $N=9.60$ .

0.3151 „ 0.1710  $BaSO_4$ .  $S=7.47$ .

$C_{21}H_{23}O_6N_2S$  requires  $N=9.44$ ;  $S=7.19$  per cent.

These numbers correspond with the formula



This sulphate separates in fine, yellow leaflets, softening at 87°, and decomposing with effervescence at 96°; it dissolves readily in water to a clear yellow solution, which is acid to litmus, and gives at once a precipitate of barium sulphate with barium chloride. The diazonium salt couples immediately with alkaline  $\beta$ -naphthol. Although stable in the dark, this salt undergoes decomposition in the light; it then darkens, becomes tarry, and evolves an odour of ethyl benzoeate.

Larger crystals of the salt can be obtained by dissolving it in alcohol and then adding the minimum amount of ether to induce crystallisation; this preparation contains 9.16 per cent. of nitrogen.

The diazotisation with nitrosyl sulphate was tried in alcoholic solution, but a less stable product was obtained, which did not give

a precipitate with aqueous barium chloride. In this case a diazonium ethylsulphate was probably produced.

*Benzoyl ethyl-4-aminonaphthalene-1-diazonium perchlorate,*  
 $N(C_2H_5)(CO \cdot C_6H_5) \cdot C_{10}H_6 \cdot N_2 \cdot ClO_4$

was obtained as a bright yellow, crystalline precipitate on mixing cold aqueous solutions of the foregoing sulphate and potassium perchlorate, the yield being about 50 per cent. of the calculated amount:

0.1342 gave 11.2 c.c.  $N_2$  at  $17^\circ$  and 771 mm.  $N = 9.82$ .

$C_{19}H_{16}O_5N_3Cl$  requires  $N = 10.45$  per cent.

The perchlorate is decomposed by warm water, yielding a viscous product; cold water hydrolyses it with the formation of a yellow, crystalline substance (compare p. 1696); it detonates with difficulty on percussion, and explodes at about  $154^\circ$ . The coupling with alcoholic  $\beta$ -naphthol takes place in the presence of a mild alkali, such as sodium carbonate or calcium hydroxide, but is inhibited by sodium or potassium hydroxide.

*Benzoyl ethyl-4-aminonaphthalene-1-diazonium stannichloride,*  
 $N(C_2H_5)(CO \cdot C_6H_5) \cdot C_{10}H_6 \cdot N_2 \cdot HSnCl_6$

separated as a bulky, yellow precipitate on mixing cold aqueous solutions of the diazonium sulphate or chloride and ammonium stannichloride:

0.1043 gave 6.5 c.c.  $N_2$  at  $20^\circ$  and 754 mm.  $N = 7.04$ .

$C_{19}H_{17}ON_3Cl_6Sn$  requires  $N = 6.67$  per cent.

The stannichloride couples directly with alkaline  $\beta$ -naphthol, and decomposes at  $154^\circ$ .

*Benzoyl ethyl-4-aminonaphthalene-1-diazonium chloride* was prepared by suspending *as*-benzoyl ethyl-1:4-naphthylendiamine in glacial acetic acid, and passing in dry hydrogen chloride until the base had dissolved to a clear pink solution. On adding successively amyl nitrite and warm dry ether, a greenish-yellow, crystalline precipitate was obtained, which, although not pure enough for analysis, gave all the reactions of the diazonium chloride. The product dissolved in cold water to a clear yellow solution; it coupled directly with alkaline  $\beta$ -naphthol, and decomposed at about  $100^\circ$ . The corresponding *diazo-cyanide*,  $N(C_2H_5)(CO \cdot C_6H_5) \cdot C_{10}H_6 \cdot N_2 \cdot CN$ , prepared by mixing dilute alcoholic solutions of the diazonium chloride or sulphate and potassium cyanide at  $-10^\circ$ , separated at once as a dark red precipitate, which, when dry, contained 16.31 per cent. of nitrogen, the calculated proportion being 17.07. The cyanide thus produced does not couple with alkaline  $\beta$ -naphthol either before or after treatment with cold concentrated sulphuric acid. The *diazonium molybdate* and *diazonium tungstate* were obtained as unstable, yellow precipitates, coupling directly with

alkaline  $\beta$ -naphthol, by mixing concentrated aqueous solutions of the diazonium sulphate and sodium molybdate and tungstate respectively.

*The Decomposition Products of Benzoylethyl-4-aminonaphthalene-1-diazonium Salts.*

1. *Hydrolysis*.—The diazonium salts from *as*-benzoylethyl-1:4-naphthylenediamine, if treated with excess of cold water or with aqueous solutions of the alkali salts of weak acids, such as sodium acetate, undergo a definite hydrolytic decomposition with the formation of a crystalline, yellow substance, which dissolves readily in concentrated hydrochloric acid, and separates unchanged in well-defined, pale yellow, felted leaflets when the acid solution is diluted with cold water. This compound, which melts at  $140^{\circ}$ , loses in weight when kept in a desiccator over phosphoric oxide. This loss is due to the removal of water, for on exposure to a moist atmosphere the desiccated product takes up water until the original weight is regained. The following analyses were made on the dried product:

0.1826 gave 0.4788  $\text{CO}_2$  and 0.0911  $\text{H}_2\text{O}$ .  $\text{C}=71.49$ ;  $\text{H}=5.54$ .

0.2077 „ 23.8 c.c.  $\text{N}_2$  at  $20^{\circ}$  and 764 mm.  $\text{N}=13.23$ .

0.1321 absorbed 0.0074  $\text{H}_2\text{O}$ .  $\text{H}_2\text{O}=5.59$ .

$\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}_3$  requires  $\text{C}=71.47$ ;  $\text{H}=5.34$ ;  $\text{N}=13.16$ ; and  $\text{H}_2\text{O}$  added requires 5.40 per cent.

These numbers correspond with the formula for a nitrosoamine,  $\text{NO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}(\text{C}_2\text{H}_5)\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , which becomes hydrated by the  $\text{NO}$  group, changing to  $\text{N}(\text{OH})_2$ . Its solution in concentrated hydrochloric acid does not contain any regenerated diazonium salt, as no coupling occurs with alkaline  $\beta$ -naphthol. The yellow alcoholic solution of this basic compound is decolorised by zinc dust and ammonium chloride, yielding a reduction product melting at  $207^{\circ}$ . Owing to the small amount of available material, the study of these substances was not carried further.

2. *Action of Ammonia*.—The diazonium salts of *as*-benzoylethyl-1:4-naphthylenediamine, when treated with aqueous ammonia, furnish a brown product, which decomposes at  $108^{\circ}$ , and does not couple with alkaline  $\beta$ -naphthol:

0.1513 gave 15.5 c.c.  $\text{N}_2$  at  $19.5^{\circ}$  and 748.5 mm.  $\text{N}=11.63$ .

$\text{C}_{38}\text{H}_{38}\text{O}_2\text{N}_5$  requires  $\text{N}=11.80$  per cent.

This result, which agrees with the formula for a diazoamine,  $\text{N}(\text{C}_2\text{H}_5)(\text{CO}\cdot\text{C}_6\text{H}_5)\cdot\text{C}_{10}\text{H}_6\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}(\text{C}_2\text{H}_5)(\text{CO}\cdot\text{C}_6\text{H}_5)$ , is confirmed by the action of cold concentrated hydrochloric acid. This

acid slowly dissolves the substance, forming a solution which now couples with alkaline  $\beta$ -naphthol.

3. *Action of Sodium Azide*.—Even in cooled solutions it was found impossible to obtain the yellow diazonium azide of *as*-benzoyl-ethyl-1:4-naphthylenediamine by the interaction of sodium azide and the diazonium sulphate. Nitrogen was evolved immediately, and colourless benzoyl-ethyl-1-aminonaphthyl-4-azoimide was produced.

A more favourable result was obtained from benzoyl-1-aminonaphthalene-4-diazonium chloride and sodium azide in well-cooled aqueous solutions. *Benzoyl-1-aminonaphthalene-4-diazonium azide*,  $C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2 \cdot N_3$ , was produced as a yellow, crystalline precipitate, practically insoluble in ice-cold water. When treated immediately with alkaline  $\beta$ -naphthol, the weight of benzoyl-1-aminonaphthalene-4-azo- $\beta$ -naphthol obtained corresponded with 75 per cent. of the amount calculated for the pure diazonium azide.

At  $0^\circ$ , and even more rapidly at higher temperatures, this yellow diazonium azide loses diazo-nitrogen, and becomes converted into the colourless azoimide.

*Benzoyl-1-aminonaphthyl-4-azoimide*,  $C_6H_5 \cdot CO \cdot NH \cdot C_{10}H_6 \cdot N_2$ , crystallises from alcohol in felted masses of colourless needles, melting and decomposing at  $167$ – $170^\circ$ :

0.0944 gave 16.3 c.c.  $N_2$  at  $20^\circ$  and 750 mm.  $N = 19.49$ .

$C_{17}H_{12}ON_2$  requires  $N = 19.45$  per cent.

This substance is remarkably sensitive to light, becoming bright yellow after a short exposure.

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

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# CLXXX.—*Dicamphorylphosphinic Acid*.

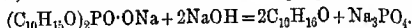
By GILBERT T. MORGAN and WALTER R. MOORE, A.R.C.S.

THE experiments described in the present communication form part of a comparative study of the organic derivatives of the phosphorus family of elements containing camphor nuclei. The condensations of sodium camphor with the trichlorides of arsenic and antimony have already been described (Trans., 1908, 93, 2144; 1909, 95,

1473; and this vol., p. 34); this paper deals with the interaction between phosphorus trichloride and sodium camphor.

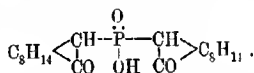
As in the earlier experiments, the condensation was effected in dry toluene, and in this case subsequent treatment with aqueous alkalis removed only one acidic substance, namely, *dicamphorylphosphinic acid*, which was shown to be monobasic by titration with standard alkali hydroxides and by the formation of a series of metallic salts.

The constitution of dicamphorylphosphinic acid was determined by alkaline hydrolysis, when it yielded camphor and sodium orthophosphate, in accordance with the following equation:



This experiment showed that dicamphorylphosphinic acid behaves like dicamphorylarsinic acid, excepting that the phosphorus compound is much more stable than its arsenic analogue towards concentrated alkali hydroxides, for it was only when the water present was removed by evaporation, and the residual alkali had fused, that the hydrolytic decomposition took place. The acid is acted on by phosphorus pentachloride with the evolution of hydrogen chloride and the formation of an acyl chloride, which is still under examination.

These experimental results demonstrate that dicamphorylphosphinic acid has the following constitutional formula:



The group relationship existing between phosphorus, arsenic, and antimony is manifested very clearly by the comparative study of their camphor derivatives. As the atomic weights of these elements increase, the tendency to form the tricamphoryl derivative increases, and the stability of the acid product diminishes. This periodic variation is summarised in the tabulation on p. 1699.

The physical and chemical properties of the metallic dicamphorylphosphinates resemble in general those of the corresponding orthophosphates. The sodium, potassium, and ammonium dicamphorylphosphinates are very soluble in water; those of the heavy metals and metals of the alkaline earths are practically insoluble; *silver dicamphorylphosphinate* is crystalline; the others are obtained as amorphous precipitates. *Lithium dicamphorylphosphinate* is also crystalline, and, like lithium phosphate, is only moderately soluble in water and alkaline solutions.

*Condensation Products from Sodium Camphor and the Trichlorides of the Phosphorus Group.*

Products.	Phosphorus trichloride.	Arsenic trichloride.	Antimony trichloride.
<i>Dicamphoryl derivatives.</i>	$(C_{10}H_{15}O)_2PO\cdot OH$ , dicamphorylphosphinic acid, stable in concentrated aqueous alkali hydroxides; decomposed by fused alkali hydroxides.	$(C_{10}H_{15}O)_2AsO\cdot OH$ , dicamphorylarsinic acid, stable in hot dilute aqueous alkali hydroxides; decomposed by very strong solutions of these alkalis.	—
<i>Tricamphoryl derivatives.</i>	—	$(C_{10}H_{15}O)_3As(OH)_2$ , tricamphorylarsinic acid is as stable towards alkalis as the above dicamphoryl derivative.	$(C_{10}H_{15}O)_3SbCl_2$ , tricamphorylstibinic chloride, slowly resolved by water into $(C_{10}H_{15}O)_3Sb(OH)_3$ , tricamphorylstibinic acid, very unstable, decomposed by dilute aqueous sodium hydroxide and even by boiling water.

*Dicamphorylphosphinic Acid,  $(C_{10}H_{15}O)_2PO\cdot OH$ .*

Sodium camphor was prepared by the method indicated by Forster (Trans., 1901, **79**, 987), using 75 grams of camphor and 75 grams of sodium. This metallic derivative was suspended in dry toluene (200 c.c.), and slowly treated with 29 grams of phosphorus trichloride diluted with two volumes of toluene. The mixture, which was thoroughly shaken, warmed up considerably, and acquired a jelly-like consistence, afterwards regaining its mobility. After one hour, the mixture was gently heated for thirty minutes, and left overnight at the ordinary temperature; 30 c.c. of water were then added to the cooled product of reaction, and the aqueous layer was separated. The toluene layer was now extracted with 2*N*-sodium hydroxide, and the cooled alkaline extract acidified with 2*N*-hydrochloric acid. The crude dicamphorylphosphinic acid thus precipitated has a tendency to become viscid. A further portion of the crude product was obtained by evaporating to dryness the first aqueous extract and the filtrate from the precipitated acid, the residue being extracted with alcohol.

Dicamphorylphosphinic acid does not crystallise so well as dicamphorylarsinic acid, and this difference recalls the behaviour of their inorganic analogues, the hydrated orthophosphoric and orthoarsenic acids, the latter being the more readily crystallisable.

Dicamphorylphosphinic acid is only sparingly soluble in water, ether, or light petroleum (b. p. 40—100°); it dissolves readily in warm benzene, toluene, chloroform, or ethyl alcohol, but only from the last of these solvents does it crystallise at all readily on cooling. The addition of light petroleum to the other solutions facilitates the separation of the acid in a crystalline condition. It separates from absolute alcohol in colourless, nodular crystals, having a prismatic habit, and decomposes at 283°. When titrated with *N*/20-sodium hydroxide, using phenolphthalein as indicator, the acid gave a molecular weight approximating to 366, the value calculated for a monobasic acid:

0.0950 gave 0.2289 CO<sub>2</sub> and 0.0731 H<sub>2</sub>O. C=65.67; H=8.61.

0.2059 „ 0.4948 CO<sub>2</sub> „ 0.1584 H<sub>2</sub>O. C=65.52; H=8.61.

0.1616 „ 0.7552 (P<sub>2</sub>O<sub>5</sub>.24MoO<sub>3</sub>). P=8.05.

0.2146 „ 1.0392 (P<sub>2</sub>O<sub>5</sub>.24MoO<sub>3</sub>). P=8.34.

C<sub>20</sub>H<sub>32</sub>O<sub>4</sub>P requires C=65.67; H=8.56; P=8.46 per cent.

A specimen of the acid obtained by repeated crystallisation from absolute alcohol when dissolved in chloroform gave the following reading in the polarimeter:

0.5963, in 25 c.c. of solvent, gave, in a 2-dm. tube,  $\alpha_D$  7.20°, whence  $[\alpha]_D^{25}$  151.1°.

It was noticed that specimens of the acid crystallised from chloroform gave lower values for  $[\alpha]_D$  of about 138.5°; repeated crystallisation from alcohol gradually raised the rotatory power to 149.7° and 151°.

*Hydrolytic Decomposition of Sodium Dicamphorylphosphinate.*—One gram of this salt was heated in a hard glass flask with excess of concentrated aqueous sodium hydroxide. No appreciable change occurred until the water present had distilled away, when, on further heating, a white sublimate appeared, which was collected in a reflux condenser, and identified as camphor (m. p. 176°); about 50 per cent. of the calculated amount was recovered, the remainder being accidentally lost. The alkaline residue was dissolved in water, and shown to contain sodium orthophosphate by the formation of yellow silver phosphate and crystalline magnesium ammonium phosphate. A small quantity of unaltered dicamphorylphosphinic acid was also recovered.

#### *Salts of Dicamphorylphosphinic Acid.*

*Sodium dicamphorylphosphinate*, (C<sub>10</sub>H<sub>16</sub>O)<sub>2</sub>PO·ONa,  $\cdot x$ H<sub>2</sub>O, was prepared by neutralising the acid exactly with pure aqueous sodium hydroxide and allowing the filtered solution to evaporate in a vacuum desiccator. The residue was a crystalline mass, very soluble

in water or alcohol. A portion of the desiccated salt was ignited with concentrated nitric acid to destroy the organic matter present, and a residue of sodium metaphosphate was finally obtained:

0.5962 gave 0.1558  $\text{NaPO}_3$ . Na=5.89.

0.5118 „ 0.1352  $\text{NaPO}_3$ . Na=5.96.

$\text{C}_{20}\text{H}_{30}\text{O}_4\text{PNa}$  requires Na=5.93 per cent.

*Ammonium dicamphorylphosphinate*,  $(\text{C}_{10}\text{H}_{15}\text{O})_2\text{PO}\cdot\text{ONH}_4\cdot x\text{H}_2\text{O}$ , produced by adding to the free acid a slight excess of aqueous ammonia and evaporating the solution over concentrated sulphuric acid, is a crystalline substance resembling the sodium salt, and very soluble in water or alcohol. The percentage amount of ammonium present corresponded with the above formula.

The following salts were obtained by double decomposition from sodium dicamphorylphosphinate.

*Lithium dicamphorylphosphinate*,  $(\text{C}_{10}\text{H}_{15}\text{O})_2\text{PO}\cdot\text{OLi}\cdot 2\text{H}_2\text{O}$ , separated in felted masses of small, colourless needles on boiling an aqueous solution of the sodium salt with slight excess of lithium chloride. The filtrate on concentration gave further quantities of this moderately soluble lithium salt, which dissolves more sparingly in warm than in cold water:

0.0734 gave 0.0164  $\text{LiPO}_3$ . Li=1.82.

0.5479 „ 0.1123  $\text{LiPO}_3$ . Li=1.68.

0.5514 „ 0.0510  $\text{H}_2\text{O}$  at  $140^\circ$ .  $\text{H}_2\text{O}$ =9.25.

$\text{C}_{20}\text{H}_{30}\text{O}_4\text{PLi}\cdot 2\text{H}_2\text{O}$  requires Li=1.71;  $\text{H}_2\text{O}$ =8.82 per cent.

The lithium was estimated by igniting the salt with nitric acid and weighing the residual metaphosphate.

*Silver dicamphorylphosphinate*,  $(\text{C}_{10}\text{H}_{15}\text{O})_2\text{PO}\cdot\text{OAg}$ , when prepared in the dark, separates in minute, white, acicular crystals, which darken on exposure to light, or on warming in their mother liquor. Weighed portions of this salt were digested with concentrated nitric acid, the solution then diluted, and titrated in the usual way with standard ammonium thiocyanate (1 c.c.=0.01109 Ag):

0.4984 required 10.3 c.c.  $\text{NH}_4\text{CNS}$  solution. Ag=22.93.

0.4190 „ 8.7 c.c. „ „ Ag=23.03.

$\text{C}_{20}\text{H}_{30}\text{O}_4\text{PAg}$  requires Ag=22.81 per cent.

*Cadmium dicamphorylphosphinate*,  $[(\text{C}_{10}\text{H}_{15}\text{O})_2\text{PO}\cdot\text{O}]_2\text{Cd}$ , prepared by double decomposition, using cadmium chloride, is a white, amorphous precipitate practically insoluble in water. Weighed portions of this salt were digested with nitric acid, the cadmium precipitated as sulphide, redissolved as nitrate or sulphate, and finally precipitated as basic carbonate:



0.5175 gave 0.0806 CdO. Cd=13.63.

0.7079 „ 0.1060 CdO. Cd=13.10.

$C_{40}H_{60}O_8P_2Cd$  requires Cd=13.38 per cent.

*Copper dicamphorylphosphinate*,  $[(C_{10}H_{15}O)_2PO\cdot O]_2Cu$ , is a blue, amorphous precipitate, insoluble in water, dissolving readily in aqueous ammonia to a deep blue solution:

0.9314 gave 0.0908 CuO. Cu=7.79.

0.7121 „ 0.0708 CuO. Cu=7.94.

$C_{40}H_{60}O_8P_2Cu$  requires Cu=8.01 per cent.

The copper was estimated in a similar manner to the cadmium in the preceding compound.

*Lead dicamphorylphosphinate*,  $[(C_{10}H_{15}O)_2PO\cdot O]_2Pb$ , is a white, amorphous precipitate obtained by the interaction of sodium dicamphorylphosphinate and lead acetate:

0.6712 gave 0.2118  $PbSO_4$ . Pb=21.57.

0.5326 „ 0.1242  $PbO$ . Pb=21.60.

$C_{40}H_{60}O_8P_2Pb$  requires Pb=22.09 per cent.

The dicamphorylphosphinates of magnesium, calcium, strontium, and barium are white, amorphous precipitates, as are also the corresponding salts of zinc, manganese, and aluminium. Mercurous, mercuric, and ferrous dicamphorylphosphinates are white, insoluble substances, the last of these becoming light yellow on exposure to the atmosphere. Ferric dicamphorylphosphinate is a light brown, gelatinous precipitate; the chromium, nickel, and cobalt salts are also insoluble, their colours resembling those of the corresponding phosphates.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

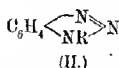
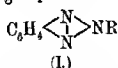
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# CLXXXI.—The Constitution of the ortho-Diazoimines. Part I. The Naphthylenediazoimines and their Benzenesulphonyl Derivatives.

By GILBERT T. MORGAN and WILLIAM GODDEN, B.Sc., A.R.C.S.

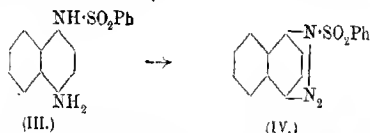
THE action of nitrous acid on an aromatic ortho-diamine or on one of its alkyl, aryl, or acyl derivatives leads to the formation of a cyclic diazo-compound, which is represented by one of the following

general formulæ, where R is either a hydrogen atom or an alkyl, aryl, or acyl group:



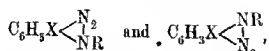
In formula I, which is due to Griess (*Ber.*, 1882, 15, 2195), the substituent R is assumed to have migrated to the nitrogen atom derived from the nitrous acid; according to formula II, proposed by Kekulé (*Lehrbuch*, II, 739), this substituent remains in the position it occupied before the triazole ring was formed.

If the latter view of their constitution be accepted, the ortho-diazoimines must be regarded as analogues of the diazoamines,  $\text{XN:N}\cdot\text{NH}\cdot\text{Y}$ , from which, however, they are distinguished invariably by their greater stability, and very frequently by their lack of colour. Moreover, certain acyl derivatives of the para-diamines, benzenesulphonyl-1:4-naphthylenediamine (III), for example, give rise to diazo-compounds (IV), produced by internal condensation, which differ very considerably from the corresponding ortho-diazoimides in being invariably coloured and also hydrolysable by acids (*Trans.*, 1906, 87, 924):



In view of these striking differences existing between the ortho- and para-diazoimides, it seemed of interest to ascertain which of the foregoing formulæ (I and II) is the more appropriate representation of the constitution of the ortho-diazoimines and their *N*-substituted derivatives.

Whichever view be adopted, it is evident that any base having the general formula  $(1)\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NHR}(2)$  can only give rise to one cyclic derivative,  $\text{C}_6\text{H}_4\cdot[\text{N}_3\text{R}]$ , but if the molecule be rendered less symmetrical by substitution in the aromatic nucleus as in  $(1)\text{NH}_2\cdot\text{C}_6\text{H}_3\text{X}\cdot\text{NHR}(2)$ , then Kekulé's hypothesis demands two isomerides:



whereas only one product will result if Griess's view be correct.

This degree of asymmetry is conveniently produced by working with ortho-naphthylene instead of ortho-phenylene derivatives. According to Kekulé's hypothesis, 1:2-naphthylenediamine and its *N*-substituted derivatives (V) should yield pairs of isomeric

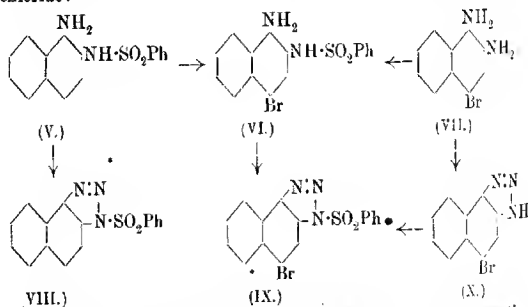
diazoimines, whereas 2:3-naphthylenediamine and 1:8-naphthylenediamine, which also furnish similar diazoimines, should each give only one product. If, however, Griess's formula be correct, only one product should be obtainable from each of these three diamines. The authors' results confirm the formulation advocated by Kekulé.

### I.—The Constitution of the *ortho*-Diazoimides.

1. Two isomeric benzenesulphonyl-4-bromo-1:2-naphthylenediamines have been prepared, differing only in the position of the benzenesulphonyl group, and these bases, on treatment with nitrous acid, furnish isomeric diazoimides. This result agrees with Kekulé's view, but is inexplicable on Griess's hypothesis.

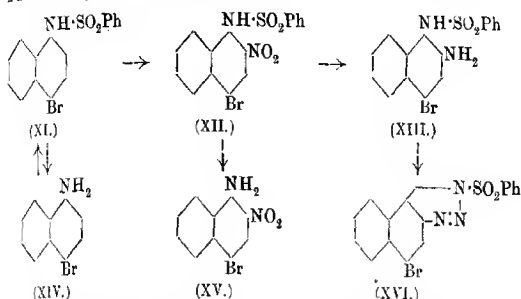
The more stable of these isomeric diazoimides is obtained by the following series of operations.

Benzenesulphonyl- $\beta$ -naphthylamine is nitrated to benzenesulphonyl-1-nitro- $\beta$ -naphthylamine, which, on reduction, gives rise to 2-benzenesulphonyl-1:2-naphthylenediamine (V). 2-Benzenesulphonyl-4-bromo-1:2-naphthylenediamine (VI) is obtained either by brominating the preceding base or by benzenesulphonating 4-bromo-1:2-naphthylenediamine (VII), this diamine being prepared from 4-bromo-2-nitro- $\alpha$ -naphthylamine (XV). These alternative methods of preparation determine the constitution of 2-benzenesulphonyl-4-bromo-1:2-naphthylenediamine (VI), and treatment of this base with nitrous acid leads to 2-benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide (IX), melting at 209°, a product which also results from 4-bromo-1:2-naphthylenediamine (VII) by successive treatment with nitrous acid and benzenesulphonyl chloride:



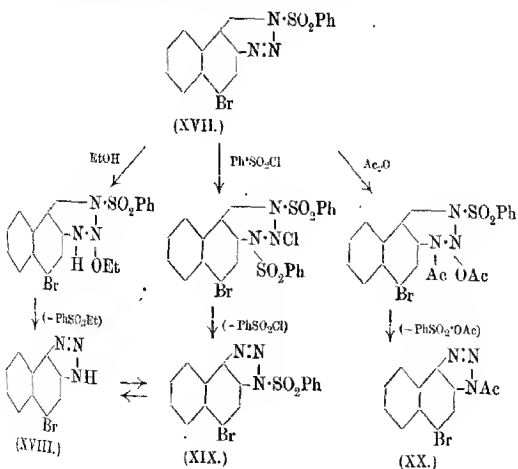
Benzenesulphonyl-4-bromo- $\alpha$ -naphthylamine (XI), the starting point in the synthesis of the less stable isomeric diazoimide, may be prepared from either benzenesulphonyl- $\alpha$ -naphthylamine or 4-bromo- $\alpha$ -naphthylamine (XIV). Nitration leads to benzenesulphonyl-

4-bromo-2-nitro- $\alpha$ -naphthylamine (XII), the position of the nitro-group being ascertained by hydrolysing the product to 4-bromo-2-nitro- $\alpha$ -naphthylamine (XV):



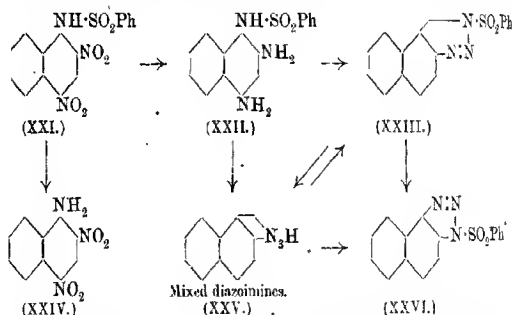
Reduction of the nitro-compound (XII) gives 1-benzenesulphonyl-4-bromo-1:2-naphthylenediamine (XIII), and nitrous acid converts this base into 1-benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide (XVI), melting at 159–160°.

The two isomeric diazoimides (IX and XVI) differ not only in melting point, but also in chemical properties. The more fusible isomeride, which contains its acyl group attached to the  $\alpha$ -nitrogen atom, is less stable, and the changes undergone by this compound may be indicated by the following diagram:



These three changes have been realised experimentally with considerable facility, and in each case the double linking has shifted from the  $\beta$ - to the  $\alpha$ -position. This molecular rearrangement is best explained by assuming that unstable additive products represent the first phase of these reactions, the second step involving respectively the loss of ethyl benzenesulphonate, benzenesulphonyl chloride, and a mixed acyl anhydride. The formation of 4-bromo-naphthylene-1-diazo-2-imine (XVIII) takes place at the ordinary temperature when the less stable isomeric diazoimide (XVII) is left in contact with a trace of alcohol. On the contrary, the more stable isomeride (XIX) is hydrolysed to the diazoimine (XVIII) only after prolonged boiling with alcoholic soda. Benzenesulphonation of the diazoimine (XVIII) regenerates the stable diazoimide (XIX), whereas acetylation yields 4-bromo-2-acetyl-naphthylene-1-diazo-2-imide (XX), which also results from the molecular change of the diazoimide (XVII) in presence of acetic anhydride.

2. The production of a less substituted pair of isomeric acylated ortho-diazoimides was a matter of considerable difficulty, which was finally solved in the following manner:



The nitration of benzenesulphonyl- $\alpha$ -naphthylamine leads to benzenesulphonyl-2:4-dinitro- $\alpha$ -naphthylamine (XXI), the position of the nitro-groups being determined by successive hydrolysis to 2:4-dinitro- $\alpha$ -naphthylamine (XXIV) and 2:4-dinitro- $\alpha$ -naphthol.

Reduction of the dinitro-compound gives the very oxidisable 1-benzenesulphonyl-1:2:4-triaminonaphthalene (XXII), and diazotisation of this base under carefully regulated conditions yields the required 1-benzenesulphonylnaphthylene-2-diazo-1-imide (XXIII), melting at 159–161°. The acyl group in this product is easily displaced, giving rise either to a mixture of the isomeric 1:2-naphthylenediazoimines (XXV) or to the more stable isomeride,

2-benzenesulphonylnaphthylene-1-diazo-2-imide (XXVI). This compound, which melts and decomposes at  $179^{\circ}$ , is more easily obtained by the action of nitrous acid on 2-benzenesulphonyl-1:2-naphthylenediamine (V).

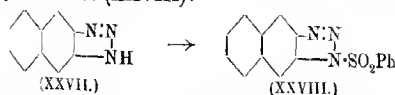
In this pair of isomerides the shifting of the double linking from the  $\beta$ - to the  $\alpha$ -position is effected less completely than in the case of the corresponding bromo-derivatives (XVII and XIX), where the bromine atom undoubtedly exerts some directive influence.

## II.—The Constitution of the ortho-Diazoimines.

The above-mentioned directive influence of the bromine atom is also noticeable in the case of 1:2-naphthylenediamine and its 4-bromo-derivative (VII); the latter base gives with nitrous acid a homogeneous product, 4-bromonaphthylene-1-diazo-2-imine (X); the former diamine yields a mixture of isomeric diazoimines, one of which is certainly naphthylene-1-diazo-2-imine, for on benzenesulphonation, the mixed diazoimines furnish a product from which 2-benzenesulphonylnaphthylene-1-diazo-2-imide (VIII and XXVI) has been isolated. The isomeric 1-benzenesulphonylnaphthylene-2-diazo-1-imide (XVII) has not been identified with certainty in this mixture of benzenesulphonyl derivatives obtained from the mixed 1:2-naphthylenediazoimines (XXV).

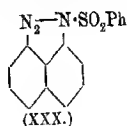
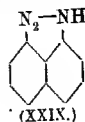
These mixed diazoimines are also obtained in an entirely different way by diazotising 1-benzenesulphonyl-1:2:4-triaminonaphthalene (XXII) in the presence of excess of alcoholic sulphuric acid, when hydrolysis of the acyl group and replacement of the para-diazonium group by hydrogen take place simultaneously. Benzenesulphonation of these mixed diazoimines leads to a mixture of benzenesulphonyl derivatives in which 2-benzenesulphonylnaphthylene-1-diazo-2-imide predominates.

Comparative experiments were then made with 2:3-naphthylene-diazoimine (XXVII), first prepared from 2:3-naphthylenediamine by Friedländer and S. von Zakrzewski (*Ber.*, 1894, 27, 764); this diazoimine is a homogeneous product, giving only one benzenesulphonyl derivative (XXVIII):



1:8-Naphthylenediamine has already been shown to form only one diazoimine (XXIX) (De Aguiar, *Ber.*, 1874, 7, 316), and its benzenesulphonyl derivative furnishes a homogeneous product, benzenesulphonyl-1:8-naphthylenediazoimide (XXX), which in colour and reactivity resembles closely benzenesulphonyl-1:4-naph-

thylenediazoimide (IV) (Morgan and Micklethwait, *Trans.*, 1906, 89, 4):



### Summary.

I. The formula (II) proposed by Kekulé for the ortho-diazoimines is supported by the following observations, most of which were made during the present investigation of the diazo-compounds of the 1:2-, 2:3-, and 1:8-naphthylenediamines and their acyl derivatives.

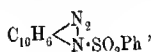
(1) 1:2-Naphthylenediamine gives rise to a mixture of diazoimines, and two benzenesulphonyl derivatives (XXIII and XXVI) of these 1:2-naphthylenediazoimines have been isolated.

(2) Two benzenesulphonyl-4-bromo-1:2-naphthylenediazoimides have been obtained, differing only in the orientation of the acyl group and double linking of the triazole ring (IX and XVI).

(3) 2:3-Naphthylenediamine furnishes only one diazoimine, which in turn gives one benzenesulphonyl derivative (XXVIII).

(4) 1:8-Naphthylenediamine and its benzenesulphonyl derivative each give only one diazo-compound (XXIX and XXX).

II. A complete series of benzenesulphonylnaphthylenediazoimides has now been prepared, the general formula being:



where  $\text{N}_2\text{N} = 1:2, 2:1, 2:3, 1:4, \text{ and } 1:8$ .

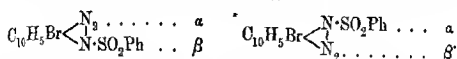
The first three (XXVI, XXVIII, and XXVIII) are ortho-diazoimides containing five-membered triazole rings; these isomerides are colourless and not hydrolysable by concentrated acids.

The last two (IV and XXX) are para- and peri-diazoimides, containing respectively seven- and six-membered triazole rings; these isomerides are yellow, and the ring undergoes fission with acids.

The strain introduced into the molecule by an increase in the number of ring-forming atoms is, in this series of compounds, accompanied by a development of colour.

EXPERIMENTAL.

1.—The Isomeric Benzenesulphonyl-4-bromo-1:2-naphthylene-diazoimides.



2-Benzenesulphonyl-4-bromo-1:2-naphthylenediamine (VI), which separated slowly on mixing chloroform solutions of bromine (1 mol.) and 2-benzenesulphonyl-1:2-naphthylenediamine (1 mol.), was washed with light petroleum and converted into its hydrochloride, this salt being then dissolved in alcohol and reprecipitated on the addition of water. The base set free with ammonia crystallised from alcohol in colourless, slender needles, melting and decomposing at 171°:

0.1778 gave 11.6 c.c. N<sub>2</sub> at 16° and 748.5 mm. N=7.49.

0.2326 „ 0.1151 AgBr. Br=21.05.

C<sub>16</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>BrS requires N=7.43; Br=21.22 per cent.

The yield of the base obtained by the foregoing method was only 30 per cent. of the calculated amount, and the bromination went even less smoothly in glacial acetic acid. The position of the bromine atom in this acylated amine was determined by preparing the base from 4-bromo-1:2-naphthylenediamine (VII) in the following way.

4-Bromo-2-nitroaceto- $\alpha$ -naphthalide (m. p. 230°) was prepared both by the nitration of 4-bromoaceto- $\alpha$ -naphthalide and by the bromination of 2-nitroaceto- $\alpha$ -naphthalide (m. p. 199°); these reactions were carried out in warm glacial acetic acid, and the former process was found to be the more convenient.

The bromo-compound (50 grams) suspended in 150 c.c. of glacial acetic acid at 80° was treated with 20 c.c. of nitric acid (D 1.42) diluted with 50 c.c. of glacial acetic acid, and previously freed from nitrous acid by the addition of a small quantity of carbamide. On hydrolysis with alcoholic ammonia, or less preferably with alcoholic potash or sulphuric acid, this bromoacetyl derivative yielded 4-bromo-2-nitro- $\alpha$ -naphthylamine (m. p. 200°), which was also prepared in quantitative yield by heating 1 gram of benzenesulphonyl-4-bromo-2-nitro- $\alpha$ -naphthylamine (XII) with 20 c.c. of alcoholic ammonia for three hours at 180°.

A singular result was obtained on attempting to hydrolyse 4-bromo-2-nitroaceto- $\alpha$ -naphthalide with alcoholic ammonia at 210° in a steel tube with leaden washers. The product, when precipitated with water and crystallised from alcohol, separated in well-defined, silvery-grey needles, melting at 224–226°, and con-



taining only 4.9 per cent. of nitrogen; this substance was also obtained on reducing with zinc dust and ammonia, some impure specimens of 4-bromo-2-nitro- $\alpha$ -naphthylamine.

4-Bromo-1:2-naphthylenediamine,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{Br}\cdot\text{NH}_2$ , was prepared by reducing pure 4-bromo-2-nitro- $\alpha$ -naphthylamine (XV) with zinc dust and ammonium chloride in hot dilute alcohol, the reducing agent being slowly introduced until the colour of the solution was discharged. The filtered solution was poured on to ice, and the precipitate, when crystallised from benzene, separated in yellowish needles, melting at  $104\text{--}106^\circ$ :

0.1487 gavo 14.95 c.c.  $\text{N}_2$  at  $18^\circ$  and 755 mm.  $\text{N}=11.53$ .

0.2124 „ 0.1672 AgBr.  $\text{Br}=33.49$ .

$\text{C}_{10}\text{H}_7\text{N}_2\text{Br}$  requires  $\text{N}=11.81$ ;  $\text{Br}=33.74$  per cent.

When dissolved in benzene containing triethylamine and treated with benzenesulphonyl chloride at  $90\text{--}100^\circ$ , 4-bromo-1:2-naphthylenediamine undergoes acylation in the  $\beta$ -amino-group only, the product (m. p.  $167\text{--}168^\circ$ ) being identical with 2-benzenesulphonyl-4-bromo-1:2-naphthylenediamine (VI, p. 1704). This result confirms the constitutional formula (*loc. cit.*) ascribed to this acylated diamine.

2-Benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide (IX,  
p. 1704).

When dissolved in cold alcohol and treated successively with concentrated hydrochloric acid (0.5 c.c.) and amyl nitrite (0.15 gram), 2-benzenesulphonyl-4-bromo-1:2-naphthylenediamine (0.5 gram) furnishes a violet precipitate which, after crystallisation from ethyl acetate and alcohol, separated in colourless, lustrous needles, melting at  $209^\circ$ :

0.1579 gavo 0.2874  $\text{CO}_2$  and 0.0356  $\text{H}_2\text{O}$ .  $\text{C}=49.64$ ;  $\text{H}=2.50$ .

0.2048 „ 19.2 c.c.  $\text{N}_2$  at  $16^\circ$  and 748.5 mm.  $\text{N}=10.76$ .

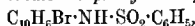
0.2452 „ 0.1176 AgBr.  $\text{Br}=20.41$ .

$\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2\text{BrS}$  requires  $\text{C}=49.48$ ;  $\text{H}=2.58$ ;  $\text{N}=10.82$ ;

$\text{Br}=20.62$  per cent.

This diazoimide was produced from both preparations of 2-benzenesulphonyl-4-bromo-1:2-naphthylenediamine, namely, that obtained by acylating 4-bromo-1:2-naphthylenediamine, and the other resulting from the bromination of 2-benzenesulphonyl-1:2-naphthylenediamine. The identical results obtained establish the constitution of the diazoimide.

*Benzenesulphonyl-4-bromo- $\alpha$ -naphthylamine*,



was prepared by the following methods.

(1) 4-Bromo- $\alpha$ -naphthylamine, obtained by brominating aceto- $\alpha$ -naphthalide and hydrolysing the bromo-derivative with concentrated aqueous potassium hydroxide, could not be converted into its benzenesulphonyl derivative by either the Schotten-Baumann reaction or Witt and Schmitt's method (p. 1714). This acylation was, however, readily effected by mixing molecular proportions of the base and benzenesulphonyl chloride in warm dehydrated pyridine, the solution being boiled for three hours. The product was extracted successively with cold dilute hydrochloric acid and warm aqueous potassium hydroxide, the benzenesulphonyl derivative being precipitated from the cooled alkaline extract by dilute acetic acid.

When crystallised from alcohol, benzenesulphonyl-4-bromo- $\alpha$ -naphthylamine separated in colourless needles with a violet tinge, the melting point being 148–149°; the yield was about 85 per cent. of the calculated amount:

0.3572 gave 12.7 c.c.  $N_2$  at 23° and 767 mm.  $N = 4.04$ .

0.4634 „ 0.2445 AgBr.  $Br = 22.21$ .

$C_{16}H_{12}O_2NBrS$  requires  $N = 3.87$ ;  $Br = 22.10$  per cent.

(2) Benzenesulphuric 4-bromo- $\alpha$ -naphthylamine was subsequently prepared by the direct bromination of benzenesulphonyl- $\alpha$ -naphthylamine, this compound, like its  $\beta$ -isomeric, being produced by Witt and Schmitt's method (p. 1714). The bromination was effected in warm glacial acetic acid, when pure benzenesulphonyl-4-bromo- $\alpha$ -naphthylamine separated.

*Benzenesulphonyl-2-nitro-4-bromo- $\alpha$ -naphthylamine,*

$C_{19}H_9Br(NO_2) \cdot NH \cdot SO_2Ph$ ,

was obtained in almost quantitative yield by shaking for two hours a mixture of two parts of the foregoing benzenesulphonyl derivative, one part of nitric acid (D 1.42), and 8–9 parts of glacial acetic acid. When crystallised from alcohol, the product separated in clusters of transparent, prismatic needles, softening at 195° and melting at 198°:

0.3302 gave 19.8 c.c.  $N_2$  at 26° and 769 mm.  $N = 6.74$ .

0.4535 „ 0.2075 AgBr.  $Br = 19.46$ .

0.2463 „ 0.1333 BaSO<sub>4</sub>.  $S = 7.43$ .

$C_{19}H_9O_4N_2BrS$  requires  $N = 6.88$ ;  $Br = 19.65$ ;  $S = 7.86$  per cent.

This nitro-compound was suspended in about 30 parts of boiling 2 per cent. acetic acid, and reduced with excess of iron filings. After neutralising the solution with sodium carbonate, the insoluble residue was extracted with alcohol.

*1-Benzenesulphonyl-4-bromo-1:2-naphthylenediamine,*

$C_{16}H_9Br(NH_2) \cdot NH \cdot SO_2Ph$ ,

was precipitated by water from the alcoholic filtrate in almost

colourless plates, and crystallised from acetic acid in colourless needles, melting and decomposing at 220° (yield, 75 per cent.);

0.3128 gave 21.5 c.c. N<sub>2</sub> at 25° and 764 mm. N=7.71.

0.3910 „ 0.1929 AgBr. Br=20.99.

C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>N<sub>2</sub>BrS requires N=7.43; Br=21.22 per cent.

This base was converted into the diazoidime (XVI) by adding successively to its alcoholic solution hydrochloric acid and amyl nitrite. On shaking, a white precipitate slowly separated, which, after crystallisation from alcohol and finally from benzene, melted at 159–160°:

0.1427 gave 0.2569 CO<sub>2</sub> and 0.0361 H<sub>2</sub>O. C=49.09; H=2.81.

0.2000 „ 19.1 c.c. N<sub>2</sub> at 20° and 744 mm. N=10.70.

0.4051 „ 0.1937 AgBr. Br=20.35.

C<sub>16</sub>H<sub>10</sub>O<sub>2</sub>N<sub>3</sub>BrS requires C=49.48; H=2.58; N=10.82;  
Br=20.62 per cent.

It was found impossible to remove bromine from this compound without producing destructive changes leading to ill-defined products.

*The Displacement of the Benzenesulphonyl Group in 1-Benzene-sulphonyl-4-bromonaphthylene-2-diazo-1-imide (compare diagram on p. 1705).*

The five-membered triazole ring in the two isomeric benzenesulphonyl-4-bromonaphthylenediazoidimes (IX and XVI), like that in the benzenesulphonyl derivatives of 1:2- and 2:3-naphthylene-diazoidimes (pp. 1715, 1718), does not undergo fission when the foregoing compounds are mixed with cold concentrated hydrochloric acid, but the acyl groups in these two isomerides are not held equally firmly in their respective triazole rings.

2-Benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide is not affected by warming with acetic anhydride or alcohol, and when crystallised from alcohol it remains unchanged at the ordinary temperature for an indefinite time. 1-Benzene-sulphonyl-4-bromonaphthylene-2-diazo-1-imide, on the contrary, readily loses its acyl group. When containing a trace of alcohol, a specimen of this substance slowly becomes viscid at the ordinary temperature, and the product, after crystallisation from alcohol, separates in colourless leaflets, containing no sulphur, and melting indefinitely at about 296°:

0.0850 gave 12.1 c.c. N<sub>2</sub> at 17° and 772.5 mm. N=16.81.

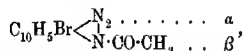
0.1370 „ 0.1030 AgBr. Br=31.99.

C<sub>16</sub>H<sub>6</sub>N<sub>3</sub>Br requires N=16.93; Br=32.25 per cent.

That this substance is 4-bromonaphthylene-1-diazo-2-imine (X) is

proved by preparing it directly from 4-bromo-1:2-naphthylene-diamine and by benzenesulphonating it, when the more stable 2-benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide (IX) is produced. This 2-benzenesulphonyl derivative undergoes hydrolysis with boiling alcoholic soda, and is again converted into 4-bromo-1:2-naphthylene-1-diazo-2-imine.

An acetylated diazoimide, 4-bromo-2-acetylnaphthylene-1-diazo-2-imide,



was obtained by boiling 1-benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide with acetic anhydride for three minutes; it crystallised from this solution in well-defined, colourless needles, melting at 158°:

0.1505 gave 18.6 c.c.  $\text{N}_2$  at 22° and 760 mm.  $\text{N} = 14.00$ .

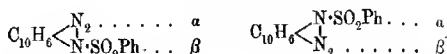
$\text{C}_{13}\text{H}_6\text{ON}_3\text{Br}$  requires  $\text{N} = 14.48$  per cent.

The position of the acetyl group was ascertained by dissolving 4-bromonaphthalene-1-diazo-2-imine (m. p. 296°) in glacial acetic acid containing acetic anhydride, and boiling the solution for one hour. On cooling, small, colourless needles separated, which melted at 158°, and did not depress the melting point of the preceding preparation.

*The Direct Conversion of 1-Benzenesulphonyl-4-bromonaphthylene-2-diazo-1-imide into 2-Benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide.*

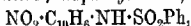
The less stable isomeride melting at 156° (XVI) was dissolved in dry benzene, and the solution boiled for two hours with excess of triethylamine and benzenesulphonyl chloride. The solution was left to evaporate at the ordinary temperature, and the residue extracted with alcohol, four fractions being collected. The first two fractions melted at 286°, and were identified as 4-bromonaphthylene-1-diazo-2-imine; the last two melted at 209°, and were identified as 2-benzenesulphonyl-4-bromonaphthylene-1-diazo-2-imide. These results show that the 1-benzenesulphonyl derivative is partially transformed by benzenesulphonyl chloride into the isomeric 2-benzenesulphonyl derivative, whilst the substance remaining unchanged is hydrolysed by the alcohol used in the extraction.

II.—*The Isomeric Benzenesulphonyl-1:2-naphthylenediazimides.*



Benzenesulphonyl- $\beta$ -naphthylamine (m. p. 104–105°), the starting point in the preparation of the former of these isomerides (VIII), was obtained by Witt and Schmitt's method (*Ber.*, 1894, 17, 2371) from  $\beta$ -naphthylamine, benzenesulphonyl chloride, and anhydrous sodium acetate, the product being purified through its sodium salt and crystallisation from alcohol or benzene.

*Benzenesulphonyl-1-nitro- $\beta$ -naphthylamine,*



is produced by shaking together the foregoing sulphonamide and a slight excess of nitric acid (D 1.42) diluted with 5 parts of warm glacial acetic acid, the reaction being completed after one or two hours. The precipitated nitro-compound, when crystallised repeatedly from hot glacial acetic acid, melts at 155.5° (yield about 90 per cent.):

0.2467 gave 17.7 c.c.  $\text{N}_2$  at 20° and 772.5 mm.  $\text{N} = 8.36$ .

0.3289 „ 0.2276  $\text{BaSO}_4$ .  $\text{S} = 9.46$ .

0.3534 „ 0.2443  $\text{BaSO}_4$ .  $\text{S} = 9.48$ .

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$  requires  $\text{N} = 8.53$ ;  $\text{S} = 9.75$  per cent.

*2-Benzenesulphonyl-1:2-naphthylenediamine (V).*

The above nitro-compound was reduced most effectively by adding slowly excess of iron filings to the substance suspended in hot 2 per cent. hydrochloric acid. After neutralising with sodium carbonate, the insoluble residue was extracted with alcohol, and the base precipitated from the filtrate by diluting with water. The product separated from alcohol in white needles, and from glacial acetic acid in stout prisms (yield 50 to 60 per cent.):

0.2759 gave 22.8 c.c.  $\text{N}_2$  at 25° and 768 mm.  $\text{N} = 9.32$ .

0.3900 „ 0.2891  $\text{BaSO}_4$ .  $\text{S} = 10.27$ .

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{S}$  requires  $\text{N} = 9.39$ ;  $\text{S} = 10.73$  per cent.

The purified base melts and decomposes at 215°, and rapidly darkens on exposure to air.

The *formyl* derivative obtained by warming the base with slightly diluted formic acid crystallised from water in colourless leaflets, melting at 176–177°.

*2-Benzenesulphonylnaphthylene-1-diazo-2-imide* (VIII).

The somewhat unstable character of the preceding base was manifested by the behaviour of its hydrochloride towards amyl nitrite in alcoholic solution, when the diazoimide produced was discoloured by a violet decomposition product. A more satisfactory result was obtained by dissolving the base in glacial acetic acid, and adding successively an equal weight of concentrated hydrochloric acid and rather more than the calculated amount of 20 per cent. aqueous sodium nitrite. The product, which was partly deposited and partly precipitated after dilution with water, crystallised from alcohol or glacial acetic acid, and melted with decomposition at 175—176°:

0.0878 gave 0.1991 CO<sub>2</sub> and 0.0289 H<sub>2</sub>O. C=61.84; H=3.65.

0.0886 „ 11.0 c.c. N<sub>2</sub> at 25° and 764 mm. N=13.93.

0.3660 „ 0.2660 BaSO<sub>4</sub>. S=9.98.

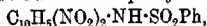
C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>S requires C=62.13; H=3.56; N=13.59;

S=10.35 per cent.

The diazoimide is very soluble in ethyl acetate, but dissolves only sparingly in benzene and other dry solvents.

*1-Benzenesulphonylnaphthylene-2-diazo-1-imide.*

*Benzenesulphonyl-2:4-dinitro-α-naphthylamine,*



was produced by nitrating benzenesulphonyl-α-naphthylamine with a moderate excess (2.5 mols.) of nitric acid (D 1.42) in five parts of glacial acetic acid. Usually the reaction proceeded in the cold even when the acyl derivative was merely suspended in the diluent, but sometimes the mixture required warming. The addition of a few drops of alcohol also served to accelerate the change.

When crystallised from alcohol, the dinitro-compound separated in felted masses of pale yellow needles, melting at 185—186°:

0.1966 gave 19.1 c.c. N<sub>2</sub> at 23° and 755.5 mm. N=10.88.

0.3341 „ 0.2113 BaSO<sub>4</sub>. S=8.68.

C<sub>16</sub>H<sub>11</sub>O<sub>6</sub>N<sub>2</sub>S requires N=11.26; S=8.57 per cent.

The position of one nitro-group in this compound was determined by preparing the substance from benzenesulphonyl-4-nitro-α-naphthylamine\* by treatment with nitric acid (D 1.42) diluted with glacial acetic acid, as in the preceding experiment.

\* This compound, which is readily prepared by adding benzenesulphonyl chloride to a cold pyridine solution of 4-nitro-α-naphthylamine, has now been found to melt at 173°, the melting point (153°) previously given being too low (Trans., 1905, 87, 928).

The position of the second group was ascertained by hydrolysing the dinitro-compound. This process was carried out in two ways. Prolonged boiling with alcoholic sulphuric acid removed the acyl group, leaving 2:4-dinitro- $\alpha$ -naphthylamine, crystallising in yellow needles, and melting at 235–238° (Meldola, *Ber.*, 1886, 19, 2683; Hühner, *Annalen*, 1881, 208, 330). More drastic hydrolysis with alcoholic soda led to the replacement of the whole henzenesulphonyl-amino-group,  $C_6H_5SO_2NH$ , by hydroxyl with the formation of 2:4-dinitro- $\alpha$ -naphthol (m. p. 143°). These reactions demonstrate conclusively the constitution of henzenesulphonyl-2:4-dinitro- $\alpha$ -naphthylamine.

1-Benzenesulphonyl-1:2:4-triaminonaphthalene (XXII).

The reduction of the preceding dinitro-compound presented considerable difficulty, owing to the very oxidisable nature of the resulting triamine.\* The best results were obtained by reducing the dinitro-compound in lots of 2 grams dissolved in 50 c.c. of alcohol and 10 c.c. of water containing 2 grams of ammonium chloride. Fresh zinc dust (4–5 grams) was added rapidly, and the mixture boiled until the yellow colour of the solution was discharged, the success of the experiment depending on the rapidity of the reduction. The solution was filtered quickly on to crushed ice in an atmosphere of carbon dioxide, and the crude triamine which separated was purified from a reddish-brown by-product by extraction with toluene. The base separated from toluene or chloroform, on adding light petroleum, in felted, colourless needles, which assumed a light brown colour on exposure to air:

0.1108 gave 13.0 c.c.  $N_2$  at 20° and 763 mm.  $N=13.48$ .

0.1585 „ 0.1224  $BaSO_4$ .  $S=10.60$ .

$C_{16}H_{13}O_2N_3S$  requires  $N=13.41$ ;  $S=10.22$  per cent.

1-Benzenesulphonyl-1:2:4-triaminonaphthalene melted at 195–197°, and dissolved readily either in acids or in aqueous alkali hydroxides, being reprecipitated from its alkaline solutions by dilute acetic acid. In aqueous solution the base was very unstable, and ferric chloride oxidised it to a red, insoluble substance.

Conversion of 1-Benzenesulphonyl-1:2:4-triaminonaphthalene into 1-Benzenesulphonylnaphthylene-2-diazo-1-imide.

After many unsuccessful attempts to diazotise 1-benzenesulphonyl-1:2:4-triaminonaphthalene without removing the acyl group, it was finally discovered that the diazotisation and elimination of the

\* The authors desire to express their thanks to Miss F. M. G. Micklethwait for her invaluable assistance in the later stages of this work.

diazo-group, could be effected in one stage by operating in the following manner. The triamine (0.4 gram) dissolved in 30 c.c. of alcohol, containing 0.3 c.c. of concentrated hydrochloric acid, was treated with excess of 33 per cent. ethyl nitrite (3 c.c.), the solution being cooled in ice and salt. After fifteen to twenty minutes, the solution, which gave no azo-reaction with alkaline  $\beta$ -naphthol, was diluted with water. The dried precipitate, when extracted with petroleum (b. p. 100–120°), separated from this solvent in light orange needles, melting at 159–161°:

0.1386 gave 0.3150  $\text{CO}_2$  and 0.0498  $\text{H}_2\text{O}$ .  $\text{C}=61.97$ ;  $\text{H}=3.99$ .

0.1070 „ 13.2 c.c.  $\text{N}_2$  at 24° and 760 mm.  $\text{N}=13.80$ .

0.2190 „ 0.1646  $\text{BaSO}_4$ .  $\text{S}=10.32$ .

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3\text{S}$  requires  $\text{C}=62.13$ ;  $\text{H}=3.56$ ;  $\text{N}=13.59$ ;  
 $\text{S}=10.35$  per cent.

1-Benzene-sulphonylnaphthylene-2-diazo-1-imide (XXII) loses its acyl group fairly readily, and the crude product of the preceding experiment always contains a certain amount of 1:2-naphthylene-diazoimine, which remains insoluble on extracting with petroleum. This diazoimine depresses the melting point of its isomeride, and differs from it in the ease with which it loses its acyl group. When warmed with alcohol, this hydrolytic change occurred, and the final product, which was then entirely soluble in aqueous sodium hydroxide, melted over a considerable range of temperature (160–190°), and thus resembled the mixed diazoimines obtained from 1:2-naphthylenediamine (p. 1719).

#### 4-Iodo- $\alpha$ -naphthylamine, $\text{C}_{10}\text{H}_7\text{I}\cdot\text{NH}_2$ .

Many unsuccessful attempts were made to prepare benzene-sulphonyl-2-nitro- $\alpha$ -naphthylamine. In one of these, 4-nitro- $\alpha$ -naphthylamine was taken as the starting point, and converted through the diazo-reaction into 4-iodo-1-nitronaphthalene (Meldola, *Trans.*, 1985, 47, 497). This compound was then reduced with zinc dust and glacial acetic acid, the 4-iodo- $\alpha$ -naphthylamine being obtained in the form of its colourless sulphate. The base itself was isolated by shaking this salt with chloroform and aqueous ammonia, when the organic solvent removed the base, which is unstable in a moist condition. The chloroform extract was quickly dried with calcium chloride, and the 4-iodo- $\alpha$ -naphthylamine precipitated by the addition of light petroleum in colourless needles, having a pink tinge; further darkening occurred on exposure to moist air:

0.4032 gave 17.3 c.c.  $\text{N}_2$  at 17° and 772.5 mm.  $\text{N}=5.06$ .

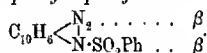
0.2352 „ 0.2042  $\text{AgI}$ .  $\text{I}=46.92$ .

$\text{C}_{10}\text{H}_7\text{NI}$  requires  $\text{N}=5.20$ ;  $\text{I}=47.21$  per cent.



4-Iodo- $\alpha$ -naphthylamine melts and decomposes at 82–84°, and slowly becomes resinous even at the ordinary temperature. It was too unstable to undergo acylation with benzenesulphonyl chloride.

*Benzenesulphonylnaphthylene-2:3-diazoimide,*



2:3-Naphthylenediamine (m. p. 195°) was prepared by heating 2:3-dihydroxynaphthalene with 10 parts of concentrated ammonia for twelve hours at 240°. In successful experiments the yield was very good, but comparatively few glass tubes could be obtained sufficiently strong to withstand the very high pressures attained at this temperature. At lower temperatures the product was mixed with 3-amino- $\beta$ -naphthol, whilst in steel tubes at higher temperatures the metal seemed to exert some reducing action on the diamine, which was thus rendered very impure.

Naphthylene-2:3-diazoimine, produced by adding the calculated amount of aqueous sodium nitrite to a solution of the diamine in very dilute hydrochloric acid, separated as a yellow precipitate, which was purified through its sodium salt and by crystallisation from light petroleum (compare Friedländer and Zakrzewski, *Ber.*, 1894, 27, 764).

This diazoimine can be benzene-sulphonated by the Schotten-Baumann reaction. The product separated as a crystalline precipitate, and was extracted with petroleum.

*Benzenesulphonylnaphthylene-2:3-diazoimide* crystallised in colourless needles, which gradually assumed an orange tinge; it melted at 156–158°:

0.1050 gave 12.5 c.c.  $\text{N}_2$  at 17° and 758 mm.  $\text{N}=13.78$ .

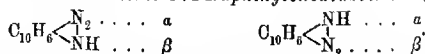
0.1492 „ 0.1146  $\text{BaSO}_4$ .  $\text{S}=10.56$ .

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_2\text{S}$  requires  $\text{N}=13.59$ ;  $\text{S}=10.35$  per cent.

The alkaline filtrate from the benzenesulphonylnaphthylene-2:3-diazoimide was acidified with dilute acetic acid, when some unchanged naphthylene-2:3-diazoimine was recovered, which melted sharply at 187°.

These experiments indicate that 2:3-naphthylenediamine yields a homogeneous diazoimine, which in turn gives only one benzenesulphonyl derivative.

### III. *The Isomeric 1:2-Naphthylenediazoimines,*



On treatment with nitrous acid or ethyl or amyl nitrite in acid solutions, 1:2-naphthylenediamine behaves quite differently from

its isomeride, 2:3-naphthylenediamine; for whereas the latter gives rise to one homogeneous substance, 2:3-naphthylenediazimine, the former diamine yields a mixed product melting over a considerable range of temperature. The earlier experiments were made with the sparingly soluble 1:2-naphthylenediamine sulphate, this salt being suspended in cold glacial acetic acid and treated with excess of 20 per cent. sodium nitrite. The salt dissolved to a brownish-yellow solution, and the best preparations of diazoimine were obtained by pouring this liquid into ice-cold water and partly neutralising the acid with dilute ammonia. The crude pale brownish-yellow product sintered at  $158^{\circ}$ , and melted at  $174^{\circ}$ :

0.1018 gave 21.0 c.c.  $N_2$  at  $17^{\circ}$  and 772 mm.  $N=24.34$ .

$C_{10}H_7N_3$  requires  $N=24.85$  per cent.

Another preparation was obtained by mixing the sulphate intimately with 20 per cent. aqueous sodium nitrite and adding the mixture to glacial acetic acid. The granular, pale brown precipitate which separated softened at  $260^{\circ}$  and melted at  $285^{\circ}$ :

0.1636 gave 35.2 c.c.  $N_2$  at  $18^{\circ}$  and 746 mm.  $N=24.38$ .

This analysis indicates that the two preparations, although differing considerably in melting point, are nevertheless isomeric; they both dissolve in aqueous sodium hydroxide, and are reprecipitated by acids in an almost colourless condition. As these products appeared to be mixtures, an attempt was made to separate their constituents by extraction with anhydrous benzene, and a soluble portion, sintering at  $150$ – $160^{\circ}$ , and melting indefinitely at  $170$ – $180^{\circ}$ , was separated from an insoluble part sintering at  $260$ – $270^{\circ}$  and melting at  $280$ – $285^{\circ}$ . Nitrogen determinations in these fractions showed, however, that partial decomposition and loss of nitrogen had occurred.

1:2-Naphthylenediamine was now prepared by reducing with stannous chloride the azo-compound, 1-sulphobenzenediazo- $\beta$ -naphthylamine,  $SO_2N \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_7 \cdot NH_2(\beta)$ . The diamine was suspended in alcohol, and treated successively with concentrated hydrochloric acid and ethyl nitrite; an evanescent green coloration developed, the solid passed into solution, and the soluble product was precipitated fractionally by the addition of iced water and sodium chloride. The first fraction sintered at  $150$ – $180^{\circ}$ , and melted indefinitely at  $210$ – $225^{\circ}$ ; the second main fraction sintered at  $100^{\circ}$ , melted at  $120^{\circ}$ , and was readily soluble in benzene. These fractions were treated with benzenesulphonyl chloride and triethylamine in dry benzene. The first fraction yielded an ill-defined product, the second gave a benzenesulphonyl derivative melting at  $175$ – $177^{\circ}$ , which was identical with 2-benzenesulphonyl-naphthylene-2-diazo-1-imide, as indicated by mixed melting points.

The diazotisation of 1:2-naphthylenediamine with sodium nitrite in dilute hydrochloric acid gave a diazoimine melting at  $110-120^{\circ}$ . This product, when benzenesulphonated, also yielded 2-benzenesulphonylnaphthylene-2-diazo-1-imide.

*The Conversion of 1-Benzenesulphonyl-1:2:4-triaminonaphthalene into the Mixed 1:2-Naphthylenediazoimines.*

One gram of the triamine dissolved in 10 c.c. of concentrated sulphuric acid, diluted with 5 grams of ice, was treated with 0.6 gram of solid sodium nitrite at  $-5^{\circ}$  to  $0^{\circ}$ . Five grams of ice were then added, and the diazonium sulphate precipitated with cooled alcohol and ether. The pale yellow salt was washed with ether and divided into two parts; one was boiled with alcohol alone, and the other with alcohol containing finely divided copper powder. In the latter case the diazonium salt was rapidly decomposed, and on cooling and diluting the solution deposited a diazoimine soluble in aqueous sodium hydroxide, and melting at  $185^{\circ}$ . The diazonium salt, when boiled with alcohol alone, resisted decomposition for a much longer time, and on cooling and diluting, a diazoimine soluble in aqueous sodium hydroxide was obtained, but in this case melting at  $265^{\circ}$ .

0.1110 gave 23.9 c.c.  $N_2$  at 749 mm. and  $19^{\circ}$ .  $N = 24.38$ .

$C_{10}H_7N_3$  requires  $N_2 = 24.85$  per cent.

This experiment was repeated several times, and similar products were obtained, with melting points ranging from  $180^{\circ}$  to  $270^{\circ}$ .

*The Benzenesulphonyl Derivatives from the Mixed 1:2-Naphthylenediazoimines.*

The mixed 1:2-naphthylenediazoimines (m. p.  $180^{\circ}$  and  $270^{\circ}$ ), prepared from 1-benzenesulphonyl-1:2:4-triaminonaphthalene, when warmed with benzenesulphonyl chloride in dry toluene containing excess of triethylamine, yielded a benzenesulphonyl derivative, melting at  $175-177^{\circ}$ , which was identical with 2-benzenesulphonyl-1-diazo-2-imide obtained directly from 2-benzenesulphonyl-1:2-naphthylenediamine.

The mixed 1:2-naphthylenediazoimines obtained from 1:2-naphthylenediamine were converted into the benzenesulphonyl derivatives by treatment with benzenesulphonyl chloride and triethylamine in boiling toluene. The product was separated into two fractions, one separating from the toluene together with the triethylamine hydrochloride, the other remaining in solution.

The less soluble fraction was crystallised from light petroleum

(b. p. 80—100°), and was then found to be identical with 2-henzenesulphonyl-1-diazo-2-imide (m. p. 177°):

0.1402 gave 0.1066 BaSO<sub>4</sub>. S=10.44.

0.1000 „ 12.1 c.c. N<sub>2</sub> at 19.5° and 750 mm. N=13.70.

C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>S requires S=10.35; N=13.59 per cent.

The more soluble fraction, after recrystallisation from light petroleum (b. p. 80—100°), separated in a mass of small, almost colourless crystals, melting somewhat indefinitely at 157—160°:

0.1662 gave 0.1290 BaSO<sub>4</sub>. S=10.63.

0.1072 „ 12.8 c.c. N<sub>2</sub> at 17° and 742 mm. N=13.53.

C<sub>16</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>S requires S=10.35; N=13.59 per cent.

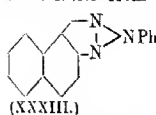
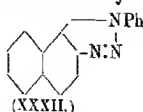
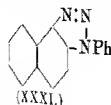
These analyses indicate that the more fusible product, obtained by benzenesulphonating the mixed 1:2-naphthylenediazoimines, is isomeric with the less fusible product, 2-henzenesulphonyl-1-diazo-2-imide.

Comparison of this more fusible product with 1-henzenesulphonylnaphthylene-2-diazo-1-imide (p. 1715) showed that the former depresses the melting point of the latter, and is probably a mixture of the two isomeric benzenesulphonyl-1:2-naphthylenediazoimides.

This view is confirmed by experiments made on the action of benzenesulphonyl chloride on 1-benzenesulphonylnaphthylene-2-diazo-1-imide in the presence of triethylamine. When these reagents are heated together in dry toluene, the product is evidently a mixed benzenesulphonyl derivative corresponding with the more fusible fraction obtained from the mixed 1:2-naphthylenediazoimines. It is evidently impossible to separate the two benzenesulphonyl derivatives by fractional crystallisation from petroleum, benzene, or other solvents, as the crystals obtained invariably consist either of the less fusible 2-henzenesulphonylnaphthylene-1-diazo-2-imide (m. p. 177°) or of mixtures of this isomeric with 1-benzenesulphonylnaphthylene-2-diazo-1-imide.

#### The Isomeric Phenyl-1:2-diazoiminonaphthalenes.

The foregoing experiments having shown that two isomeric diazoimines are possible corresponding with the formulæ XXXI and XXXII, an attempt was made to synthesise the latter from the



base described by A. Harden as 1-phenyl-1:2-naphthylenediamine (*Ber.*, 1886, 19, 343; *Annalen*, 1889, 255, 161). The product

obtained by this author's process did not correspond in composition with this diamine, and it was not affected by nitrous acid or amyl nitrite.

The isomeride (XXXI) has already been described by Zincke and Campbell (*Annalen*, 1889, 255, 344); it was prepared for purposes of comparison by adding 20 per cent. aqueous sodium nitrite to a glacial acetic acid solution of the purified hydrochloride of 2-phenyl-1:2-naphthylendiamine (m. p. 138—140°). After repeated crystallisation from benzene, the colourless product melted at 143—144°. (Found, C=78.09; H=4.76; N=16.67. Calc., C=78.36; H=4.40; N=17.14 per cent.)

During the course of this investigation, Noelting, Grandmougin, and Freimann (*Ber.*, 1909, 42, 1377) have given the formula XXXII to a diazoimine obtained as a by-product in the reduction of benzene-2-azo- $\alpha$ -naphthyl benzoate and the alkyl ethers of benzene-2-azo- $\alpha$ -naphthol. This mode of formation does not, however, afford definite evidence of the constitution of the diazoimine.

In addition to these diazoimines (XXXI and XXXII), a third isomeric triazole (XXXIII) was formerly obtained by Zincke and Lawson, who prepared it by oxidising benzeneazo- $\beta$ -naphthylamine (*Ber.*, 1885, 18, 798 and 3132). The relationship of these isomeric triazoles is still under investigation (*Proc.*, 1910, 26, 151).

The authors desire to express their thanks to the Research Grant Committees of the Royal Society and Chemical Society for grants which have partly defrayed the expenses of this investigation.

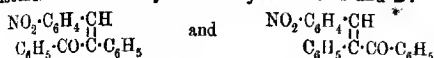
ROYAL COLLEGE OF SCIENCE, LONDON,  
SOUTH KENSINGTON, S.W.

# CLXXXII.—Action of Light on the Stereoisomeric Piperonylideneacetones and on other Unsaturated Ketones.

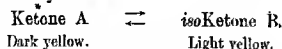
By HANS STOBBE and FORSYTH JAMES WILSON.

In a recent paper (*Annalen*, 1910, 374, 237) we have shown that isomeric ketones of the type of benzylidenedecybenzoin,  $\text{Ar}\cdot\text{CH}:\text{CPh}\cdot\text{COPh}$ , can be converted into one another by heating them to their melting points and above, by the action of traces of hydrochloric acid, or by the action of sunlight on their benzene

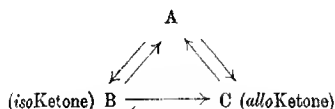
solutions in presence of iodine. These transformations lead to a state of equilibrium which, for example, in the case of the two stereoisomeric *o*-nitrobenzylidenedeoxybenzoins A and B:



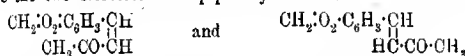
can be represented by the scheme:



The equilibrium for the three isomeric yellow *p*-nitrobenzylidenedeoxybenzoins A, B, and C can be illustrated diagrammatically as follows:



On account of these results, we thought it advisable to study, on these lines, other unsaturated ketones of the benzylidenacetone and benzylidenacetophenone series. The ketones first investigated were the two stereoisomeric piperonylidenacetones:



which were first prepared by Haber (*Ber.*, 1891, 24, 618). We designate them with the letters A and B. The ketone A, obtained synthetically from piperonal and acetone, is yellow, and melts at 107°; the isoketone B (m. p. 111°), obtained from A by crystallisation from a quantity of boiling water insufficient to dissolve it entirely, is white. While therefore under these conditions (at about 100°) the yellow ketone A is converted into the white ketone B, the isoketone B is transformed, as Haber has already shown, into the ketone A by heating to 190°.

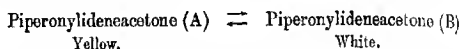
The following experiments were made in order to ascertain how the two ketones behave towards light.

*Experiment I.*—A solution of the yellow piperonylidenacetone (4 grams) in a solution of iodine in benzene (0.1 gram of iodine in 100 grams of benzene) was exposed to the action of direct sunlight for five weeks in March and April; it gradually became darker in colour. After shaking with sodium thiosulphate solution to remove the iodine, and evaporation, a dark mass was obtained which, after recrystallisation from alcohol in the presence of animal charcoal, yielded, in addition to much unaltered ketone A, only 0.7 gram of the white isoketone B.

*Experiment II.*—A solution of the white isoketone B (1.2 grams)

in a 0.1 per cent. solution of iodine in chloroform was exposed to the action of direct sunlight. After a week's exposure in summer, the solution was worked up as in experiment I; the product consisted almost exclusively of the yellow ketone A, besides a very small amount of unaltered isoketone B.\*

These experiments show that the two isomeric ketones, like the ketones of the benzylidenedeoxybenzoin type, are interconvertible—that light influences the two reciprocal processes indicated by the scheme:



Even if as yet these experiments have not been carried out under similar conditions,\* and conclusions as to the state of equilibrium cannot yet be drawn, nevertheless the deeper coloured ketone A appears to be more stable when in the molten state than the white isoketone B, and also to be more stable in solution towards light.

Other unsaturated ketones, anisylideneacetone, piperonylideneacetophenone, anisylideneacetophenone, and *o*-methoxybenzylidenacetophenone,† could not be converted into their hitherto unknown stereoisomerides either by a five weeks' exposure of their iodine-benzene solutions to direct sunlight, or by boiling these solutions for twelve hours in diffused daylight. In all these experiments the substances were for the most part recovered unaltered, and to a smaller extent they were converted into yellow, red, or brown resins, from which homogeneous products could not be obtained. These ketones therefore are probably stable towards sunlight, and could perhaps be converted into their labile stereoisomerides only by light of a different wave-length, for example, by ultra-violet rays (compare Störmer, *Ber.*, 1909, 42, 4865). We intend to carry out these experiments in suitable solutions, and hope to communicate the results later.

Doubly unsaturated ketones, for example, cinnamylideneacetophenone,  $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , behave quite differently

\* In one experiment, when the isoketone B in iodine-benzene solution was exposed to sunlight for a week during summer, the only product obtained was a resin.

† *o*-Methoxybenzylidenacetophenone,  $\text{C}_6\text{H}_4(\text{OMe})\text{CH}:\text{CH}\cdot\text{COPh}$ , was prepared by condensing *o*-methoxybenzaldehyde (15 grams) and acetophenone (13.3 grams) in 70 grams of alcohol and 20 grams of sodium hydroxide solution (10 per cent.). It separates from the solution as an oil which soon solidifies, especially on rubbing, and a further amount (bringing the yield to 80–90 per cent. of the theoretical) can be obtained by adding water to the solution. It crystallises from light petroleum in pale yellow, felted needles, which melt at 58–59°:

0.1205 gave 0.3558  $\text{CO}_2$  and 0.0687  $\text{H}_2\text{O}$ .  $\text{C}=80.52$ ;  $\text{H}=6.33$ .

$\text{C}_{16}\text{H}_{14}\text{O}_2$  requires  $\text{C}=80.67$ ;  $\text{H}=5.88$  per cent.

The substance is readily soluble in alcohol, ether, or benzene.

from the simple unsaturated ones. This ketone is converted by the action of sunlight, not only into a stereoisomeride, but also into a polymeric ketone. An account of these investigations will be published shortly by H. Stobbe and Konrad Rücker.

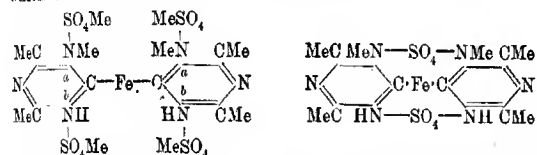
THE UNIVERSITY,  
LEIPZIG.

GLASGOW AND WEST OF SCOTLAND TECHNICAL  
COLLEGE, GLASGOW.

### CLXXXIII.—*Tetramethyl Ferrocyanide and some Derivatives.*

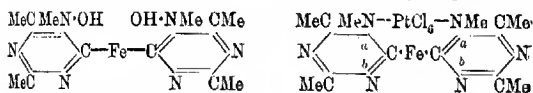
By ERNALD GEORGE JUSTINIAN HARTLEY.

In a recent communication (this vol., p. 1066) the author showed that methyl sulphate reacts with dry potassium ferrocyanide, and two salts (I) and (II)\* were obtained of a hypothetical base (III), which was itself too unstable to be isolated:



(I.) Hexamethyl ferrocyanogen dihydrogen methyl sulphate.

(II.) Hexamethyl ferrocyanogen dihydrogen sulphate.



(III.) Hypothetical Base.

(IV.) Hexamethyl ferrocyanogen platinumchloride.

In these compounds two pairs of nitrogen atoms exhibit basic functions, but of an extremely weak nature in the case of that pair (*b, b*) which are not directly attached to methyl groups. Consequently the salts (I) and (II) give a strongly acid reaction in aqueous solution, whilst in the platinumchloride (IV), which is formed from either of them, only the more basic pair (*a, a*) is combined with the acid radicle.

It was considered probable that the acid groups  $\text{MeHSO}_4$  in (I), which are attached to the less basic pair of nitrogen atoms (*b, b*), were produced by moisture absorbed by the methyl sulphate mainly during filtration, when a hot-water funnel was used.

\* These formulae are only put forward provisionally, as the constitution of the ferrocyanogen radicle is still uncertain. They are, however, in this case, very serviceable for representing the relationship between the various substances described.



Further experiments have since been made, in which greater care was taken to avoid the introduction of water vapour, when the reaction followed a somewhat different course and other products were isolated, but the complete account of their formation is still somewhat obscure.

In order to ensure the absence of moisture in the materials used, the potassium ferrocyanide (20 grams), freshly precipitated from aqueous solution by means of alcohol for each experiment, was heated to  $105^{\circ}$  for forty-eight hours, and the methyl sulphate (150 c.c.) was distilled under diminished pressure just before use.

The reaction was accompanied by rather marked changes of colour, the mixture turning bright yellow after about one hour's heating, and then becoming purple. At the end of five hours the liquid was filtered, taking care to prevent it from coming in contact with moisture from the air. On cooling, a crop of purple crystals (about 3 grams) was deposited, which differed from those previously obtained at the same stage in the reaction (described as B, *loc. cit.*, p. 1068) in being soluble in ethyl alcohol and giving no precipitate with barium chloride. They were recrystallised from ethyl alcohol, when they lost a great part of the colouring matter (which appears to be of the nature of Prussian blue). This substance undergoes no change when kept in an exhausted desiccator over sulphuric acid; it is extremely hygroscopic, and forms a neutral solution in water, which gives the same platinichloride as (I) and (II). When dissolved in ethyl alcohol and treated with concentrated sulphuric acid, the acid sulphate (II) is precipitated. It is evidently therefore a salt of the base (III), and the analytical numbers show it to be the methyl sulphate, as was anticipated from its mode of formation:

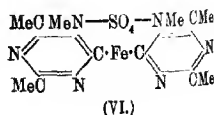
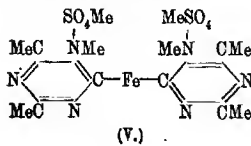
0.2782 gave 0.0437  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=11.00$ .

0.2512 „ 0.2942  $\text{CO}_2$  and 0.1059  $\text{H}_2\text{O}$ .  $\text{C}=31.96$ ;  $\text{H}=4.71$ .

0.3272 „ 0.0504  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}=10.78$ .

The second determination of iron was made with material crystallised a second time from alcohol and quite colourless.

These numbers correspond with the formula  $\text{C}_{14}\text{H}_{10}\text{O}_5\text{N}_6\text{S}_2\text{Fe}$ , or  $(\text{CH}_3)_6\text{FeC}_6\text{N}_6(\text{CH}_3\text{SO}_4)_2$ , which requires  $\text{C}=32.04$ ,  $\text{H}=4.61$ ,  $\text{Fe}=10.68$  per cent. Applying the same nomenclature as before, this would be called hexamethyl ferrocyanogen methyl sulphate, and may be represented by (V):



The methyl sulphate solution, from which the above crystals had been removed, was then subjected to distillation under diminished pressure. There was at first a slight evolution of gas, which, however, soon ceased, after which the distillation was continued until no more liquid passed over, the final temperature being varied in different experiments from  $80^{\circ}$  to  $130^{\circ}$ . The residue (about 18 grams) in each case contained a portion which was almost insoluble in ethyl alcohol, and proved on analysis to be identical with (II); it differed in quantity, but was usually about one-third of the total weight of residue. The other portion was soluble in alcohol, and was deposited on evaporating the solution in slightly purple crystals always contaminated with some of (II), from which it could be freed by a second crystallisation. These crystals resembled the substance (V) in being extremely hygroscopic, neutral to litmus in aqueous solution, and in giving the same platinumchloride (IV) and acid sulphate (II) under similar conditions. With barium chloride they gave no precipitate. In some cases they separated with alcohol of crystallisation, which was only very slowly given off in a vacuum. It was then found better for analytical purposes to redissolve in alcohol and precipitate with ether, when they were obtained as a fine, crystalline powder free from combined alcohol. They lose practically no weight at  $100^{\circ}$  in a vacuum, but when heated to this temperature in an ordinary air-bath they are hydrolysed by the moisture in the air and converted completely into (II), the presence of two  $\text{SO}_4$  groups in the molecule being thereby proved.

The analytical numbers were as follows:

1. Substance twice crystallised from ethyl alcohol:

0.2196 gave 0.0324  $\text{Fe}_2\text{O}_3$ .  $\text{Fe} = 10.33$ .

0.1803 „ 0.2218  $\text{CO}_2$  and 0.0812  $\text{H}_2\text{O}$ .  $\text{C} = 33.57$ ;  $\text{H} = 5.04$ .

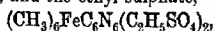
2. Substance crystallised once from ethyl alcohol and afterwards redissolved and precipitated with ether:

0.2839 gave 0.0418  $\text{Fe}_2\text{O}_3$ .  $\text{Fe} = 10.31$ .

0.1266 „ 0.1575  $\text{CO}_2$  and 0.0569  $\text{H}_2\text{O}$ .  $\text{C} = 33.95$ ;  $\text{H} = 5.03$ .

These numbers, together with the chemical properties of the substance, point to its being a mixture of the methyl and ethyl sulphates of the base (III).

The methyl sulphate,  $(\text{CH}_3)_6\text{FeC}_6\text{N}_6(\text{CH}_3\cdot\text{SO}_4)_2$ , requires  $\text{C} = 32.04$ ,  $\text{H} = 4.61$ ,  $\text{Fe} = 10.18$ ; and the ethyl sulphate,



requires  $\text{C} = 34.77$ ,  $\text{H} = 5.10$ ,  $\text{Fe} = 10.14$  per cent.

It is somewhat difficult to explain the presence of the ethyl groups. An examination of the methyl sulphate used, both by a combustion and by an analysis of the potassium salt ( $\text{KMeSO}_4$ )

produced by hydrolysis with alcoholic potash, gave no indication of the presence of a substance with a higher percentage of carbon or hydrogen. It seems more likely to be the result of a slight decomposition of the methyl sulphate during the long heating which the process requires, similar to that which takes place when this ester is distilled under atmospheric pressure. The products of this decomposition are presumably ethylene and sulphuric acid or methylsulphuric acid, and a partial recombination of the two former would result in the formation of some ethylsulphuric acid.

The production of some sulphuric acid in this way would also account for the considerable proportion of (II) always found, which in this case can hardly be due to the introduction of moisture during the experiment.

In consequence of the ease with which both the methyl sulphate (V) and the supposed mixture of methyl and ethyl sulphate can be quantitatively converted into the readily purified acid sulphate (II) by precipitation with sulphuric acid in alcoholic solution, and especially as this latter has proved to be the best starting point for additional derivatives, it was considered a waste of time to make further experiments with a view to separating the mixture into its constituents.

It was shown in the previous paper that the substance (I) is very readily converted into (II) by the loss of two molecules of methyl sulphate, this transformation taking place either by heating, or even at the ordinary temperature on keeping for some days in an exhausted desiccator over sulphuric acid.

It might be expected that the neutral methyl sulphate (V) would behave in a similar manner, and by the loss of one molecule of methyl sulphate becomes a sulphate as represented by (VI), but this does not appear to be the case, since no trace of the latter compound is found amongst the products of the reaction just described, even when a temperature of  $130^{\circ}$  was reached, and there is no loss of weight when the pure salt (V) is kept in a vacuum.

Although the sulphate (VI) is not formed from (V) as was expected, it can be prepared from (II) as follows. When baryta is added to an aqueous solution of the latter until the liquid is just neutral to litmus, the  $\text{H}_2\text{SO}_4$  group is eliminated. On filtering from barium sulphate and evaporating to dryness in a vacuum over sulphuric acid, a white, extremely hygroscopic solid is left, which differs from the original salt in being readily soluble in ethyl alcohol, from which it separates in cubes apparently containing alcohol of crystallisation, since, on keeping for only a short time over sulphuric acid in an exhausted desiccator, they become opaque and fall to a white powder. The substance is quite neutral in

aqueous solution, but is very unstable, soon turning yellow and decomposing, even when kept in a desiccator, and it is extremely difficult to obtain it in a suitable condition for analysis. When it has acquired a constant weight in a vacuum it still apparently retains about one molecule of alcohol, which it loses on heating with a certain amount of decomposition.

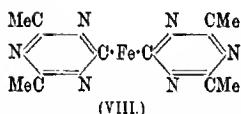
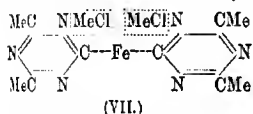
A determination of Fe and  $\text{SO}_4$ , with material dried to a constant weight in a vacuum, gave the following numbers:

0.2196 gave 0.0417  $\text{Fe}_2\text{O}_3$ . Fe = 13.29.

0.2646 „ 0.1337  $\text{BaSO}_4$ .  $\text{SO}_4$  = 20.79.

The loss of weight at  $100^\circ$  was 9.83. Calculating the percentages of Fe and  $\text{SO}_4$  from the weight of salt left after heating, this gives Fe = 14.74,  $\text{SO}_4$  = 23.06.  $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_6\text{SFe}$  requires Fe = 14.06,  $\text{SO}_4$  = 24.10 per cent.  $\text{C}_{12}\text{H}_{18}\text{O}_4\text{N}_6\text{SFe} + \text{C}_2\text{H}_6\text{O}$  contains  $\text{C}_2\text{H}_6\text{O}$  = 10.36 per cent.

These figures, together with the fact that the substance gives the platinumchloride (IV), may be regarded as sufficient evidence for the above constitution, and as the corresponding chloride is far more stable and readily obtained pure, it was not considered advisable to sacrifice material in the attempts to obtain the sulphate in a more favourable condition for analysis.



The chloride (VII) is also prepared from (II) by neutralising with baryta as above, and then adding a slight excess of barium chloride, filtering, and evaporating in a vacuum, when a white, crystalline mass is left and is extracted with ethyl alcohol. On adding ether to the alcoholic solution, hexamethyl ferrocyanogen chloride (VII) is precipitated as a very bulky, white, crystalline precipitate. This is not nearly so hygroscopic as the sulphate, and does not appear to decompose at all on keeping:

0.3252 gave 0.2476  $\text{AgCl}$ . Cl = 18.82.

0.5780 „ 0.1242  $\text{Fe}_2\text{O}_3$ . Fe = 15.04.

$\text{C}_{12}\text{H}_{18}\text{N}_6\text{Cl}_2\text{Fe}$  requires Cl = 18.99. Fe = 15.00 per cent.

#### *Preparation of Tetramethyl Ferrocyanide.*

When the above chloride is heated under diminished pressure, a steady evolution of gas begins to take place at about  $140^\circ$ , and is completed at this temperature after two to three hours.

The gas was collected over mercury and tested; it burnt with a green flame, and a few drops of water shaken up in the tube

in which the combustion had taken place were found to contain hydrochloric acid. The gas was therefore presumably methyl chloride.

The residue had scarcely altered in appearance from the original salt, and showed no signs of fusion; it had an odour resembling that of isocyanides, which it lost on keeping for some time in a vacuum; it was free from chlorine, and was readily soluble in chloroform, alcohol, or water, and insoluble in ether or acetone.

It resembles tetrachyl ferrocyanide prepared from silver ferrocyanide and ethyl iodide in its solubility and in giving in aqueous solution a white precipitate with mercuric chloride, a reddish-purple colour with ferric chloride, and a yellow, microcrystalline precipitate with platinic chloride.

An analysis gave numbers showing it to be tetramethyl ferrocyanide:

0.2352 gave 0.0694  $\text{Fe}_2\text{O}_3$ .  $\text{Fe} = 20.66$ .

0.2057 „ 0.3309  $\text{CO}_2$  and 0.0808  $\text{H}_2\text{O}$ .  $\text{C} = 43.90$ ;  $\text{H} = 4.39$ .

$\text{C}_{10}\text{H}_{12}\text{N}_6\text{Fe}$  requires  $\text{Fe} = 20.56$ ;  $\text{C} = 44.09$ ;  $\text{H} = 4.44$  per cent.

Its formation is evidently due to the loss of the two molecules of methyl chloride (shown in (VII) enclosed by dotted lines).

In order to obtain it quite pure, the best procedure is to dissolve it in chloroform, when a rather dark-coloured solution is formed, owing to a slight amount of decomposition during the heating. On gradually adding ether, the colouring matter is first precipitated, and can be filtered off. The substance is afterwards thrown down by a further addition of ether as an almost colourless precipitate. By repeating the process it can be obtained quite colourless. It is then crystallised from chloroform, from which it separates in large, light yellow, transparent, rectangular plates, containing chloroform of crystallisation, which is given off fairly rapidly at the ordinary temperature, and completely at about  $60^\circ$  in a few hours. A determination of iron was made on some material purified in this way and heated to  $65^\circ$  until a constant weight was obtained, and afterwards to  $105^\circ$ , when there was no further loss. 0.2729 gave 0.0801  $\text{Fe}_2\text{O}_3$ ;  $\text{Fe} = 20.55$ . Calc.,  $\text{Fe} = 20.56$  per cent. Tetramethyl ferrocyanide crystallises from water in yellowish-white aggregates, which appear amorphous, but when magnified are seen to consist of fine needles.

On strongly heating, it decomposes without melting, giving off an alkaline vapour, and leaving a residue of pure ferric oxide.

The original object of this research was to prepare tetramethyl ferrocyanide, and to determine its molecular weight in aqueous solution in order to ascertain whether this agreed with the double formula which was found to represent best the properties of

calcium ferrocyanide (*Phil. Trans.*, 1909, A, 209, 319). For this purpose it is proposed to make a series of determinations of the osmotic pressure of its solutions when sufficient material is available.

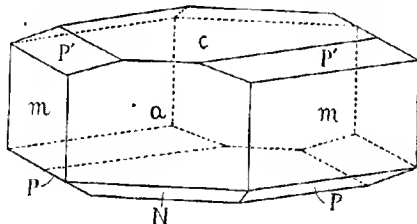
In conclusion, I wish to express again my thanks to Lord Berkeley, to whom I am greatly indebted for placing at my disposal his laboratory and all the apparatus and materials for continuing this research, and for the interest he has taken in its progress.

FOXCOMBE LABORATORY,  
• NR. OXFORD.

#### Appendix.

Mr. W. H. Barrett, of Balliol College, Oxford, kindly undertook an examination of the crystallographic properties of the acid sulphate (II). His description and measurements are herewith given as follows:

Small, yellow crystals from methyl alcohol, which soon begin to turn opaque. They can be obtained again transparent on recrystallisation from methyl alcohol. They are usually combinations of  $a\{100\}$ ,  $c\{001\}$ ,  $m\{110\}$ , and  $N\{10\bar{1}\}$ , and in habit either tabular parallel to  $c\{001\}$ , or



elongated along the  $b$  axis, as in the drawing. On some crystals, forms  $P\{112\}$  and  $P'\{113\}$  were present, but on only one crystal were they sufficiently well developed to give measurable images of the goniometer signal. Nine crystals selected from two crops were measured, but many of the reflexions were too blurred to be of any value, and so the readings corresponding to these were discarded.

*System*: Monoclinic holosymmetric.

*Habit*: Tabular parallel to  $c\{001\}$ , or prisms elongated along the  $b$  axis.

*Forms observed*:  $c\{001\}$ ,  $a\{100\}$ ,  $N\{10\bar{1}\}$ ,  $m\{110\}$ ,  $P\{112\}$ ,  $P'\{113\}$ .

*Axial ratio*:  $a:b:c = 1.9101 : 1 : 2.0472$ ;  $\beta = 93.91^\circ$ .

Table of Angles.

Measured angle.	No. of angles.	No. of crystals.	Limits.	Mean.	Calculated.
$\alpha : \bar{c} \{001\} : (\bar{1}00)$	14	8	92°49'—93° 8'	93° 1'	—
$c : N' \{001\} : (\bar{1}01)$	5	5	48 19 —48 48	48 36	—
$\alpha : m \{100\} : (110)$	23	6	62 16 —62 35	62 26	—
$c : P \{001\} : (\bar{1}12)$	4	1	49 41 —49 52	49 46	49°54
$c : P' \{001\} : (113)$	1	1	47°13'	47 13	46 50

Optical properties: The acute bisectrix coincides with the  $b$  axis; and the plane of the optic axes lies in the obtuse angle  $\beta$ , and is inclined to the  $a$  axis at an angle of about  $30^\circ$ , as shown by the extinction on a plate ground approximately parallel to (010). The optic axial angle is rather small, and the axes have a slight dispersion in the sense  $s > v$ . The crystal was too brittle to allow of making a section sufficiently thin to enable the sign of the birefringence or any dispersion of the bisectrices to be determined, but compensation of a crystal viewed through  $c\{001\}$  shows that the birefringence must be positive.

The behaviour of the crystals in turning opaque is peculiar. The opacity starts from the two  $c$  faces, and, viewed through the  $a$  face, the opaque part resembles in form two pyramids whose summits gradually interpenetrate, and whose bases are the  $c$  faces. The opaque part has thus somewhat of an hour-glass shape.

CLXXXIV.—*The Relation of Position Isomerism to Optical Activity. Part VIII. The Rotation of the Menthyl Esters of the Alkyloxy- and Alkylamino-derivatives of Benzoic Acid.*

By JULIUS BEREND COHEN and HAROLD WARD DUDLEY.

In previous investigations on this subject (Trans., 1903, **83**, 1214; 1904, **85**, 1262, 1271; 1905, **87**, 1190; 1906, **89**, 49, 460, 1479) the active esters submitted to optical examination included halogen, nitro- and nitro-halogen derivatives of benzoic acid. The results derived from the study of nine separate series of compounds clearly indicated that, with the single exception of the ortho-isomeride of the iodobenzoic esters,\* the ortho-substituent had the greatest

\* We propose to study the effect of temperature on the rotation of the three isomeric iodobenzoic esters,

influence in diminishing the rotation, as in the halogen derivatives, or in increasing it, as in the nitro-compounds, and that substituents in the meta- and especially in the para-position had a very subordinate effect. In the following table we have limited ourselves to reproducing the four series of mono-derivatives of the benzoic esters, as the presence of two substituents bears a close relation to that of the single atom or group:

Menthyl ester.	[M] <sub>D</sub> <sup>20°</sup> .			[M] <sub>D</sub> <sup>100°</sup> .
	Cl.	Br.	I.	
Ortho.....	-195.0°	-205.5°	-246.0°	-381.0°
Meta.....	237.0	238.5	234.5	251.0
Para.....	237.5	237.0	241.0	225.0

Menthyl benzoate, [M]<sub>D</sub><sup>20°</sup> - 239°.

*Positive Groups.*—It will be observed that the compounds examined contain only negative substituents. The only observations on active esters of benzoic acid containing positive groups are those of Tschugaëff (*Ber.*, 1898, **31**, 1775), who examined the menthyl esters of the three toluic acids, to which the following values are assigned:

Ortho, [M]<sub>D</sub><sup>20°</sup> - 231.2°    Meta, [M]<sub>D</sub><sup>20°</sup> - 270.8°    Para, [M]<sub>D</sub><sup>20°</sup> - 252.4°

Here the order of rotation is the reverse of that given above; for although the value of the ortho-compound is rather less than that of menthyl benzoate, that of the para-compound is much higher.

We have repeated these observations at 20° and 100° with carefully prepared specimens of the three esters. They were examined both before and after distillation. Distillation under diminished pressure produced no measurable change in rotation.

The values for the ortho- and meta-compounds are practically the same as those obtained by Tschugaëff, but that of the para-compound is much below his number. The previous order remains nevertheless unaltered:

Menthyl ester.	[M] <sub>D</sub> <sup>20°</sup> .	[M] <sub>D</sub> <sup>100°</sup> .
Ortho.....	-231.0°	-223.0°
Meta.....	240.0	234.5
Para.....	246.5	237.0

*Effect of Temperature.*—An interesting feature in these observations is the effect produced on the rotation by rise of temperature. The relatively large decrease in the value of the para-compound at 100° brings the meta- and para-compounds within a few units of one another. This value at the higher temperature is especially noteworthy when compared with that of menthyl benzoate at the same temperature. In former comparisons with menthyl benzoate we have taken Tschugaëff's value, [M]<sub>D</sub><sup>20°</sup> - 236.3°;



but this was obtained in benzene solution, whereas, with very few exceptions, we have examined the fused substances without solvent. It seemed desirable to ascertain the value for fused menthyl benzoate. This has been effected first at 100°, and then by supercooling (the substance melts at 54°) at about 20°, with the following result:

	20°.	100°.
[M].....	- 239°	- 233°

If now we compare the values of the menthyl toluates with that of menthyl benzoate at the higher temperature, the old order is reproduced, in which the rotation of the meta- and para-compounds approximates to that of the unsubstituted ester. The question of temperature obviously plays a very important rôle when instituting a comparison between the rotational values of a compound and its derivatives, a matter which demands more attention than it has so far received.

The number of observations on the effect of temperature on the rotation of fused substances is not very large. A list of most of them, references to which are given in the foot-note below,\* has been collected by Walden (*Ber.*, 1905, 38, 363, 382), who, without throwing any light on the cause of these changes, merely states "da der Temperaturcoefficient abhängig ist von der Constitution der activen Substanz, so dürfte er in der Folge eine grössere Beachtung verdienen als bisher." Winther (*Zeitsch. physikal. Chem.*, 1906, 55, 259) has found an empirical formula which gives values in close agreement with the observed results. But it is difficult to discover any apparent relation between temperature-coefficient and constitution in the different series, for even among isomeric compounds the value in the case of one isomeride may be positive with rise of temperature, in that of another, negative, and in a third it may fluctuate. As an illustration we may give the observations on the three menthyl nitrobenzoates (Cohen and Armes, *Trans.*, 1905, 87, 1190):

t.	[M] <sub>D</sub>		
	Ortho.	Meta.	Para.
100°	379°	- 250°	- 230°
80	380	253	232
70	379	252	233
65	381	251	237.5
40	—	251	—
20	—	252	—

\* Frankland and Wharton, *Trans.*, 1896, 69, 1587; Frankland and Patterson, *ibid.*, 1898, 73, 199; Frankland and McCrae, *ibid.*, 1898, 73, 307; Patterson and McCrae, *ibid.*, 1900, 77, 1107; Patterson, *ibid.*, 1904, 85, 765, 1133; Patterson and Taylor, *ibid.*, 1905, 87, 34; Patterson and Kaye, *ibid.*, 1906, 89, 1884; 1907, 91, 708; Winther, *Zeitsch. physikal. Chem.*, 1908, 45, 331; 1906, 55, 259; 56, 703; 1907, 60, 566, 590; Walden, *Ber.*, 1905, 38, 363.]

The temperature-coefficients in the case of the ortho- and para-compounds are negative, whilst in that of the meta-compound it fluctuates. The values in all cases are small. But when we turn to the alkyloxy-esters, we find that the effect of temperature is very marked, as may be seen from the following table:

Menthyl ester.	[M] <sub>D</sub> <sup>20°</sup>			[M] <sub>D</sub> <sup>100°</sup>		
	o.	m.	p.	o.	m.	p.
Methoxybenzoic acid.....	-148.0°	-247.5°	-250.5°	-155.0°	-242.5°	-238.5°
Ethoxybenzoic „ .....	solid	244.0	solid	157.5	237.5	238.5
Propoxybenzoic „ .....	170.5	240.5	-250.0	180.0	235.0	234.0
Isopropoxybenzoic acid....	169.0	—	246.0	176.0	—	233.5
isoAmyloxybenzoic „ ...	187.0	240.5	247.5	196.0	237.5	234.0
Allyloxybenzoic „ ...	—	—	252.0	175.0	—	237.0
Benzoyloxybenzoic „ ...	168.5	—	255.0	159.0	—	239.0
Methoxynaphthoic „ ... (β) 166.5	—	—	(α) 256.0 (β) 159.0	—	(α) 239.0	—

Menthyl benzoate, [M]<sub>D</sub><sup>20°</sup> - 239°, [M]<sub>D</sub><sup>100°</sup> - 233°.

Whilst the temperature-coefficients of the ortho-compounds are small, and for the most part positive with rise of temperature, those of the para-compounds are large and negative, whilst those of the meta- are the smallest of the three and negative. The general result is that at the higher temperature the rotational values of the meta- and para-compounds approximate, like those of the toluic esters, to the value of menthyl benzoate. It appears therefore that in comparing the activity of position isomerides, two factors have to be considered, namely, the change in rotation due to structure, and that produced by the physical condition of the compounds under examination. The question then arises; which is to be regarded as the standard temperature? If we take the higher temperature, the rule which is applicable to the esters with negative substituents holds equally in the case of those with positive groups, that is to say, the ortho-substituent has the greatest influence, and the meta- and para-substituents a very subordinate effect.\*

If, according to Winther (*loc. cit.*), change of rotation in a compound is conditioned by change in internal pressure, it seems probable that a temperature widely removed from the crystallising point, and therefore from the region in which molecular aggregates may be formed, will afford a more correct basis for comparison.

It is for this reason that provisionally we are disposed to regard the values at 100° as the more satisfactory for the purpose of comparison until more light has been thrown on this aspect of the

\* The rule laid down by Frankland and Wharton (*Trans.*, 1896, 69, 1309, 1583), in which the para-isomeride is supposed to exert the greatest effect, is not only contradicted by some of their own and others observations, but seems quite incapable of proof where solvents are used, owing to the indeterminate influence of the solvent.

problem. Another fact in support of our view of the influence of contiguous groups on the rotational value of the active group, is that furnished by menthyl phenylacetate. This substance, which is isomeric with the menthyl toluates, exhibits both in its mobile character (the toluates are very viscid liquids) as well as in its rotation a much closer resemblance to the aliphatic than to the aromatic esters (Rupe, *Annalen*, 1909, **369**, 311, 927):

	$[M]_D^{20}$		$[M]_D^{20}$
Menthyl <i>o</i> -toluate .....	-231.0°	Menthyl phenylacetate ..	-185°
" <i>m</i> -toluate .....	240.0	" propionate .....	160
" <i>p</i> -toluate .....	246.5	" butyrate .....	160

*Dimethylaminobenzoic Esters*.—The ortho- and para-esters were obtained in the form of viscid liquids of a red colour, which could neither be crystallised nor distilled without decomposition. The only criterion of purity was the analysis, the fact that the acid chloride of *p*-dimethylaminobenzoic acid yielded with methyl alcohol the pure methyl ester (m. p. 102°), and that the menthyl ester was unchanged in composition and in rotation after precipitation from solution in light petroleum as the hydrochloride. Seeing that the acid chlorides have a deep orange colour, and the menthyl esters retain the red colour after reprecipitation as hydrochlorides, we are inclined to think that the colour is the natural physical attribute of these esters, although by analogy we should have anticipated a different result, the acids themselves being quite colourless.

Owing to the very viscid nature of the esters, it was difficult to ascertain their densities at 20°, and the rotations have only been determined at 100°:

	$[M]_{100}^{100}$
Menthyl ortho-dimethylaminobenzoate .....	-101°
" para-dimethylaminobenzoate .....	253

Assuming that these values represent an approximation to the true values of the pure substances, the result is interesting, for although the rotation of the para-compound is about 20° higher than the mean of the other para-compounds, the difference produced by the dimethylamino-group in the ortho-position is nearly triple this amount.

For convenience of reference, the following table of densities and specific and molecular rotations at 20° and 100° are collected together.

Menthyl ester.	$\alpha_D^{20}$ .	$\alpha_D^{100}$ .	$[\alpha]_D^{20}$ .	$[\alpha]_D^{100}$ .	$[\text{M}]_D^{20}$ .	$[\text{M}]_D^{100}$ .
<i>o</i> -Methoxybenzoic ester.....	1.045	0.9823	-51.08°	-53.37°	-148.2°	-154.7°
<i>m</i> -Methoxybenzoic „ .....	1.034	0.9766	85.39	83.69	247.0	242.7
<i>p</i> -Methoxybenzoic „ .....	1.036	0.9766	86.47	82.30	250.7	238.6
<i>o</i> -Ethoxybenzoic „ .....	solid	0.9641	—	51.75	—	157.3
<i>m</i> -Ethoxybenzoic „ .....	1.017	0.9582	80.20	78.10	244.0	237.4
<i>p</i> -Ethoxybenzoic „ .....	solid	0.9622	—	78.39	—	238.3
<i>o</i> -Propoxybenzoic „ .....	1.019	0.9589	53.59	56.63	170.4	180.1
<i>m</i> -Propoxybenzoic „ .....	1.010	0.9511	75.65	73.93	240.6	235.1
<i>p</i> -Propoxybenzoic „ .....	1.016	0.9569	78.66	73.60	250.1	234.0
<i>o</i> - <i>iso</i> Propoxybenzoic ester...	1.034	0.9760	53.08	56.54	168.8	175.7
<i>p</i> - <i>iso</i> Propoxybenzoic „ .....	1.011	0.9514	77.42	73.37	246.1	233.3
<i>o</i> - <i>iso</i> Amyloxybenzoic „ .....	1.003	0.9442	54.01	56.69	188.8	196.2
<i>m</i> - <i>iso</i> Amyloxybenzoic „ .....	0.9947	0.9363	69.53	68.66	210.6	237.6
<i>p</i> - <i>iso</i> Amyloxybenzoic „ .....	0.9954	0.9400	71.57	67.57	247.3	233.8
<i>o</i> -Allyloxybenzoic ester.....	solid	0.9689	—	55.35	—	174.9
<i>p</i> -Allyloxybenzoic „ .....	1.027	0.9689	79.69	74.95	251.8	236.9
<i>o</i> -Benzyloxybenzoic ester:						
(PCl <sub>5</sub> )	1.147	1.069	44.89	42.28	164.3	154.7
(SOCl <sub>2</sub> )	1.142	1.083	47.07	44.49	172.3	162.8
<i>p</i> -Benzyloxybenzoic ester ..	1.064	1.0015	69.68	65.29	255.1	238.9
<i>o</i> -Dimethylaminobenzoic ester .....	—	1.019	—	33.29	—	100.9
<i>p</i> -Dimethylaminobenzoic ester .....	—	0.9852	—	85.13	—	257.9
<i>o</i> -Methoxynaphthoic ester...	1.076	1.022	78.27	70.32	266.2	239.0
<i>m</i> -Methoxynaphthoic „ .....	1.083	1.025	48.94	46.84	166.4	159.2
<i>p</i> -Benzyloxynaphthoic ester	1.118	1.058	87.27	77.82	363.0	324.4
<i>o</i> -Toluic ester .....	0.9982	0.9383	84.35	81.41	231.1	223.1
<i>m</i> -Toluic „ .....	0.9946	0.9352	87.59	85.03	240.0	234.7
<i>p</i> -Toluic „ .....	0.9937	0.9336	89.93	80.56	246.4	237.2
Phenylacetic ester .....	1.002	0.9400	68.70	65.56	183.2	179.6
Benzoic ester .....	1.002	0.9417	91.95	69.47	239.0	232.7

*Melting Points of the Acids.*—The melting points of the alkyloxybenzoic acids which have been ascertained in the course of this investigation are collected in the following table:

				<i>iso</i>			
Acid.	Methoxy.	Ethoxy.	Propoxy.	<i>iso</i> Propoxy.	Amyloxy.	Allyloxy.	Benzyloxy.
Ortho	99—101°	19—20°	low m. p.	liquid	liquid	60—62°	76—77°
Meta	104—105	137	71—72°	—	74—75°	—	—
Para	180—182	195—196	145—147	160—163°	141—142	160—162	188—190°

It will be seen that the melting point rises from the ortho- to the para-compound. This is quite in accordance with other observations on the melting points of the three position isomerides. For example, the three series of halogen benzoic acids exhibit a similar relationship:

Acid.	Chlorobenzoic.	Bromobenzoic.	Iodobenzoic.
Ortho.....	137°	148°	162°
Meta .....	152	155	183
Para .....	236	251	265

*Melting Points of the Menthyl Esters.*—There is very little regularity to be observed in the melting points of the menthyl esters. They are for the most part viscid liquids of low melting point, and their viscid character when fused is probably accountable

for the fact that many of them do not crystallise readily, and that a few have not yet been obtained in the solid form:

Menthyl ester.	Methoxy.	Ethoxy.	Propoxy.	isoAmyloxy.	Allyloxy.
Ortho .....	42°	52—53°	40—41°	liquid	61—62°
Para .....	liquid	76—77	34—35	54—55°	liquid

*Reaction Temperature of the Acid Chloride and Menthol.*—In the course of preparing the menthyl esters by heating the acid chloride with menthol, we have taken occasion to note approximately the temperature at which the reaction appeared to begin. This was done by observing the first appearance of bubbles of hydrogen chloride in the liquid. Although the reaction temperatures cannot be regarded as very accurate, the results seem to us to possess a certain interest, on account of the uniformly lower temperature at which the ortho-compound reacts. This is exactly the reverse of the behaviour of the ortho-halogen and nitro-compounds, which require a higher temperature to bring about combination (Cohen, *Trans.*, 1906, **89**, 1482). Seeing that the unsubstituted benzoyl chloride requires a temperature of 83° to initiate the reaction with menthol, it is clear that the alkyloxy-group in the ortho-position facilitates combination. These observations have a direct bearing on the subject of steric hindrance, and furnish another example of the fact that the nature rather than the position of a particular group adjoining the reacting group determines the character of the process (Cohen and McCandlish, *Trans.*, 1905, **87**, 1261):

Acid chloride.	Ortho.	Meta.	Para.
Toluoyl chloride .....	68°	97°	78°
Methoxybenzoyl chloride.....	69	90	100
Ethoxybenzoyl „ .....	37	70	120
Propoxybenzoyl „ .....	48	100	79
isopropoxybenzoyl „ .....	60	—	78
isoAmyloxybenzoyl „ .....	66	93	105
Allyloxybenzoyl „ .....	57	—	85
Benzoyloxybenzoyl „ .....	75	—	100
Methoxynaphthoyl „ .....	(a) 37	(B) 85	—
Benzoylnaphthoyl „ .....	88	—	—

#### EXPERIMENTAL.

The general method for preparing the alkyloxy-esters of menthol was to convert the hydroxy-acid into the methyl ester, and act on this with sodium methoxide and the alkyl iodide in alcoholic solution. The alkyloxy-ester was then hydrolysed with aqueous or alcoholic sodium hydroxide or potassium hydroxide, and the acid separated. The alkyloxy-acid was next converted into the acid chloride by means of phosphorus pentachloride, or in a few cases by thionyl chloride, and the resulting acid chloride heated with menthol. The excess of menthol was then removed by distillation

in steam, and the product extracted with ether, shaken with sodium carbonate to remove free acid, and the menthyl ester finally separated. In the case of the meta- and para-methoxy- and ethoxy-acids, it was possible to convert the hydroxy-acids directly into these compounds by employing methyl and ethyl sulphate; but the latter do not react at all with the ortho-hydroxy-acids, nor with the  $\alpha$ - and  $\beta$ -hydroxynaphthoic acids.

The preparation of the menthyl esters of ortho- and meta-methoxybenzoic acid are fully described by way of illustration, but in the subsequent preparations, which are mainly repetitions of the same process, only such details as the properties of the products and the yields are given.

The analyses are collected together in a table at the end.

*Menthyl o-Methoxybenzoate*,  $C_8H_4(OMe) \cdot CO_2 \cdot C_{10}H_{19}$ .—Thirty grams of methyl salicylate, 4.5 grams of sodium in 100 c.c. of methyl alcohol, and 30 grams of methyl iodide were heated in a flask with reflux condenser for several hours. The greater part of the alcohol was then removed on the water-bath and the residue poured into water, which was rendered alkaline with sodium hydroxide to dissolve unaltered methyl salicylate, and extracted with ether. The ethereal extract was dehydrated, the ether removed, and the residue distilled under diminished pressure. The methoxy-ester boils at  $140-144^\circ/15$  mm.; yield 25 grams. It was hydrolysed with 100 c.c. 10 per cent. sodium hydroxide solution, giving 18 grams of acid melting at  $99-101^\circ$ . Twelve grams of the acid were heated with 16 grams of phosphorus pentachloride on the water-bath. The phosphoryl chloride was removed as far as possible on the water-bath under diminished pressure and in a current of dry air. Without distilling the residual acid chloride (13 grams), which partly decomposes even at a low pressure, it was heated with an equal weight of menthol. The reaction began at about  $60^\circ$ , and was completed by heating for two hours at  $130^\circ$ . The product, after distillation in steam to remove menthol, solidified, and was digested with sodium carbonate solution to remove free acid and filtered. The yield of crude product (m. p.  $38-40^\circ$ ) was 22 grams. It was recrystallised from alcohol, and melted at  $42^\circ$ . Owing to its low melting point and tendency to superfusion, it is very difficult to crystallise from any solvent, and usually separates as an oil, remaining liquid for days, even when cooled in a freezing mixture.

The rotation of the ester in a 3.02-cm. tube was then determined, and it was then distilled under diminished pressure. It boiled at  $222-226^\circ/12$  mm., the main portion distilling at  $226^\circ$ . On cooling, it solidified and melted at  $38-40^\circ$ . The rotation of the distillate was determined, and gave somewhat lower results.

The rotation of another specimen in which the acid chloride was distilled without decomposition, and which gave a rather purer product is entered in the last column:

	Before distillation.	After distillation.	Specimen 11 (undistilled).
$\alpha_D^{20}$ .....	- 15.95°	- 15.10°	- 16.12°
$\alpha_D^{100}$ .....	15.65	14.90	15.84

Specimen 11:  $d_4^{20} = 1.045$ ;  $d_4^{100} = 0.9823$ ;  $l = 3.02$  cm.

$[\alpha]_D^{20} = -51.08^\circ$ ;  $[\alpha]_D^{100} = -53.37^\circ$ .

$[M]_D^{20} = -148.2^\circ$ ;  $[M]_D^{100} = -154.7^\circ$ .

*Menthyl m-Methoxybenzoate*.—27.6 Grams of *m*-hydroxybenzoic acid, 200 c.c. of 10 per cent. sodium hydroxide solution, and 24 c.c. of methyl sulphate were boiled for two and a-half hours. The liquid was then cooled and extracted with ether to remove impurities. After removing the ether, the liquid was acidified with hydrochloric acid, which precipitated the acid. Twenty-one grams of acid were obtained, which, after recrystallisation from boiling water, melted at  $104.5^\circ$ . It was converted into the acid chloride, and, after careful removal of the phosphoryl chloride, was heated with menthol without previous distillation. The reaction began at about  $90^\circ$ , and proceeded slowly. After separation of the free menthol and acid, as described above, the ester was obtained as a viscid liquid with a pale yellow colour. It distilled at  $236\text{--}237^\circ/30$  mm., and gave a colourless distillate. A second distilled specimen is entered in the last column:

	Before distillation.	After distillation.	Specimen 11 (distilled).
$\alpha_D^{20}$ .....	- 26.70°	- 26.25°	- 26.58°
$\alpha_D^{100}$ .....	24.70	24.10	—

Specimen I, before distillation:  $d_4^{20} = 1.034$ ;  $d_4^{100} = 0.9766$ ;  $l = 3.02$  cm.

$[\alpha]_D^{20} = -85.39^\circ$ ;  $[\alpha]_D^{100} = -83.69^\circ$ .

$[M]_D^{20} = -247.6^\circ$ ;  $[M]_D^{100} = -242.7^\circ$ .

*Menthyl p-Methoxybenzoate*.—The para-compound was prepared in exactly the same manner as the meta-compound. The methoxy acid melts at  $180\text{--}182^\circ$ . The reaction between the acid chloride and menthol began a little above  $100^\circ$  and proceeded vigorously. Nine grams of acid gave 9.5 grams of acid chloride and 15 grams of crude ester. The ester resembles the meta-compound. It is a viscid liquid with a faint yellow colour, which boils at  $229\text{--}230^\circ/15$  mm., and gives a colourless distillate. Another distilled specimen is entered in the last column:

	Before distillation.	After distillation.	Specimen 11 (distilled).
$\alpha_D^{20}$ .....	27.08°	27.05°	26.92°
$\alpha_D^{100}$ .....	24.30	24.27	—

Specimen I:  $d_4^{20} = 1.036$ ;  $d_4^{100} = 0.9766$ ;  $l = 3.02$  cm.

$[\alpha]_D^{20} = -86.47^\circ$ ;  $[\alpha]_D^{100} = -82.30^\circ$ .  
 $[\text{M}]_D^{20} = -250.7^\circ$ ;  $[\text{M}]_D^{100} = -238.6^\circ$ .

*Menthyl o-Ethoxybenzoate*,  $\text{C}_6\text{H}_4(\text{OEt})\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ .—The ortho-ester was prepared in exactly the same manner as the corresponding methoxy-derivative, using ethyl iodide in place of methyl iodide. The colourless ethoxy-ester distilled at  $180\text{--}185^\circ/113$  mm. The ethoxy-acid melts at  $19\text{--}20^\circ$ , but owing to its low melting point it is difficult to crystallise, and cannot be distilled undecomposed. It was therefore converted directly into the acid chloride. Sixty grams of salicylic ester gave the same weight of ethoxy-ester, from which 50 grams of ethoxy-acid were obtained. Seventeen grams of the acid gave 22 grams of acid chloride and 33 grams of crude ester. The reaction with menthol began at  $37^\circ$ , and was completed in two to three hours at  $100^\circ$ . The menthyl ester crystallises in colourless prisms from alcohol (m. p.  $52\text{--}53^\circ$ ). It could not be supercooled to  $20^\circ$ . Two specimens were prepared, and the mean of the rotations taken for calculation.

	Specimen I.	Specimen II.
$\alpha_D^{100}$ .....	$15.00^\circ$	$15.09^\circ$

Mean:  $d_4^{100} = 0.9641$ ;  $l = 3.02$  cm.

$[\alpha]_D^{100} = -51.75^\circ$ ;  $[\text{M}]_D^{100} = -157.3^\circ$ .

*Menthyl m-Ethoxybenzoate*.—The ester was prepared in the same manner as the *m*-methoxy-ester, using ethyl sulphate in place of methyl sulphate. The acid melts at  $137^\circ$ . It was converted into the acid chloride, which distilled without decomposition at  $135\text{--}140^\circ/16$  mm., and solidified on cooling. It crystallises from light petroleum in long prisms, melting at  $27\text{--}28^\circ$ . When heated with menthol the action began about  $70^\circ$ . After purification, the ester consisted of a pale yellow oil, which distilled undecomposed at  $230^\circ/18$  mm. Fifteen grams of acid gave 14.5 grams of acid chloride and 22 grams of ester. Two specimens were prepared, and the mean of the rotations taken for calculation:

	Specimen I.	Specimen II.
$\alpha_D^{20}$ .....	$-24.99^\circ$	$-24.33^\circ$
$\alpha_D^{100}$ .....	$22.92$	$22.23$

Mean:  $d_4^{20} = 1.017$ ;  $d_4^{100} = 0.9582$ ;  $l = 3.02$  cm.

$[\alpha]_D^{100} = -80.26^\circ$ ;  $[\alpha]_D^{20} = -78.10^\circ$ .  
 $[\text{M}]_D^{20} = -244.6^\circ$ ;  $[\text{M}]_D^{100} = -237.4^\circ$ .

*Menthyl p-Ethoxybenzoate*.—The ester was obtained in the same manner as the *m*-ethoxy-compound. The acid melted at  $195\text{--}196^\circ$ . The acid chloride is a colourless liquid, which distils undecomposed



at 160°/20 mm. On heating with menthol, the action began at 130°, and the mixture was maintained at 140° for two hours. Twelve grams of acid gave 9 grams of acid chloride and 12 grams of ester.

The ester, after distillation in steam, solidified, and was re-crystallised from alcohol (m. p. 76–77°). It distils undecomposed at 230–235°/16 mm. Two specimens were prepared, and gave the following rotations:

	Specimen I.	Specimen II.
$\alpha_D^{100}$ .....	-22.73°	-22.83°
Mean: $d_4^{100} = 0.9623$ ; $l = 3.02$ cm.		
$[\alpha]_D^{100} = -78.39^\circ$ ; $[M]_D^{100} = -238.3^\circ$ .		

*Menthyl o-Propoxybenzoate*,  $C_6H_4(O \cdot C_3H_7) \cdot CO_2 \cdot C_{10}H_{19}$ .—The propoxy-methyl ester was obtained from methyl salicylate and propyl iodide in the usual way, and distilled at 157–163°/45 mm. After hydrolysis with 20 per cent. sodium hydroxide solution, the acid was precipitated as an oil of very low melting point, which could not be recrystallised, and was not further purified. It was converted directly into the acid chloride, which distilled at 147–155°/12–15 mm. The reaction with menthol began at 48°. The menthyl ester was obtained as a solid, which crystallised from methyl alcohol in lustrous leaflets, melting at 40–41°. Only one specimen was prepared:

$\alpha_D^{20} = -16.50^\circ$ ; $\alpha_D^{100} = -16.40^\circ$ .
$d_4^{20} = 1.019$ ; $d_4^{100} = 0.9689$ ; $l = 3.02$ cm.
$[\alpha]_D^{20} = -53.5^\circ$ ; $[\alpha]_D^{100} = -56.63^\circ$ .
$[M]_D^{20} = -170.4^\circ$ ; $[M]_D^{100} = -180.1^\circ$ .

*Menthyl m-Propoxybenzoate*.—Fifty grams of *m*-hydroxybenzoic acid were boiled with 150 c.c. of methyl alcohol and 10 c.c. of concentrated sulphuric acid, and yielded 46 grams of ester, melting at 68–70°. The ester was boiled with one equivalent of sodium in 170 c.c. of methyl alcohol, and one equivalent of propyl iodide. The crude ester weighed 55 grams, and distilled at 159–161°/15 mm., yielding 44 grams of pure, colourless product. The ester yielded 33 grams of acid, crystallising in long prisms, melting at 71–72°. The acid gave an equal weight of acid chloride, which distilled without decomposition at 155–160°/18 mm., and solidified on cooling. It melted at 26–28°. The action with menthol began at 100°. Sixteen grams of acid chloride gave 22 grams of ester, which distilled undecomposed at 235°/18 mm.:

$\alpha_D^{20} = -23.09^\circ$ ; $\alpha_D^{100} = -21.23^\circ$ .
$d_4^{20} = 1.010$ ; $d_4^{100} = 0.9511$ ; $l = 3.02$ cm.
$[\alpha]_D^{20} = -75.65^\circ$ ; $[\alpha]_D^{100} = -73.93^\circ$ .
$[M]_D^{20} = -240.6^\circ$ ; $[M]_D^{100} = -235.1^\circ$ .

*Menthyl p-Propoxybenzoate*.—Methyl *p*-propoxybenzoate was prepared in the usual way, and was obtained as a pale yellow oil, having a peculiar, garlic-like odour (b. p. 165—170°/40 mm.). It solidified on cooling, and melted at 15°. The acid obtained on hydrolysis crystallised from alcohol in colourless, glistening plates, melting at 145—147°. The acid chloride, which had a green colour, distilled at 145—150°/12 mm. The action with menthol began at 79°. The menthyl ester crystallised from methyl alcohol in tufts of colourless needles, melting at 34—35°:

$$\begin{aligned} \alpha_D^{20} &= -24.12^\circ; \alpha_D^{100} = -21.27^\circ. \\ d_4^{20} &= 1.016; d_4^{100} = 0.9569; l = 3.02 \text{ cm.} \\ [a]_D^{20} &= -78.66^\circ; [a]_D^{100} = -73.60^\circ. \\ [M]_D^{20} &= -250.1^\circ; [M]_D^{100} = -234.0^\circ. \end{aligned}$$

*Menthyl o-isopropoxybenzoate*.—Methyl *o*-isopropoxybenzoate is a colourless oil, boiling at 140—145°/16 mm. Only 58 per cent. of the theoretical quantity of ester was obtained, part of the original methyl salicylate being hydrolysed in the process. The acid was obtained as an oil, which did not crystallise, nor could it be purified by conversion into a salt. It was therefore converted into the acid chloride without purification. The acid chloride was a brown liquid which could not be distilled. It was heated directly with menthol. The action began at 60°, and the menthyl ester obtained was a dark red, viscid liquid, which was only partly decolorised by animal charcoal. On attempting to distil the ester, a pale yellow and much more mobile liquid was collected at 205—212°/9 mm., but apparently some decomposition had occurred, as a dark residue remained in the distilling flask. Subsequent analysis showed that both the undistilled and distilled portions contained a small quantity of phosphorus. The dark colour of the acid chloride also pointed to a secondary action between the acid chloride and the phosphorus chloride or oxychloride, and two other preparations failed to give an ester free from phosphorus. The rotations of these specimens were higher than those of the other ortho-compounds, no doubt owing to the presence of phosphorus compound. The following observations were made with the distilled ester:

$$\begin{aligned} \alpha_D^{20} &= -16.58^\circ; \alpha_D^{100} = -16.29^\circ. \\ d_4^{20} &= 1.034; d_4^{100} = 0.9766; l = 3.02 \text{ cm.} \\ [a]_D^{20} &= -53.08^\circ; [a]_D^{100} = -56.54^\circ. \\ [M]_D^{20} &= -168.8^\circ; [M]_D^{100} = -175.7^\circ. \end{aligned}$$

*Menthyl p-isopropoxybenzoate*.—Methyl *p*-isopropoxybenzoate is a colourless oil, boiling at 159—162°/15 mm. The yield was 70 per cent. of the theory. The *p*-propoxy-acid crystallised from spirit in colourless needles, melting at 160—163°. The acid chloride was

best obtained by the action of phosphorus pentachloride in benzene solution. The reaction with menthol began about 78°. The ester crystallised from alcohol in colourless crystals, melting at 57—58°:

$$\begin{aligned} \alpha_D^{20} &= -23.64^\circ; \alpha_D^{100} = -21.08^\circ. \\ d_4^{20} &= 1.011; d_4^{100} = 0.9514; l = 3.02 \text{ cm.} \\ [\alpha]_D^{20} &= -77.42^\circ; [\alpha]_D^{100} = -73.37^\circ. \\ [M]_D^{20} &= -246.1^\circ; [M]_D^{100} = -233.3^\circ. \end{aligned}$$

*Menthyl o-isoAmyloxybenzoate*,  $C_6H_4(O \cdot C_5H_{11}) \cdot CO_2 \cdot C_{10}H_{19}$ .—Methyl *o*-isoamyloxybenzoate is a nearly colourless oil, boiling at 160—164°/14 mm., the yield being about 45 per cent. of the theory. The isoamyloxy-acid, which was obtained as an amber-coloured oil, was purified by recrystallisation of its calcium salt. The acid chloride was prepared with phosphorus pentachloride in benzene solution, and decomposes on distillation under diminished pressure. The reaction with menthol began at 66°, and the resulting ester was a pale brown, viscid liquid:

$$\begin{aligned} \alpha_D^{20} &= -16.35^\circ; \alpha_D^{100} = -16.16^\circ. \\ d_4^{20} &= 1.003; d_4^{100} = 0.9442; l = 3.02 \text{ cm.} \\ [\alpha]_D^{20} &= -54.01^\circ; [\alpha]_D^{100} = -56.69^\circ. \\ [M]_D^{20} &= -186.8^\circ; [M]_D^{100} = -196.2^\circ. \end{aligned}$$

*Menthyl m-isoAmyloxybenzoate*.—Methyl *m*-isoamyloxybenzoate is an oil which distils at 185°/16 mm. The acid, after recrystallisation from alcohol, melted at 74—75°. The acid chloride was prepared in benzene solution, and consisted of a brown liquid which could not be distilled. The action with menthol began at 93°, and was completed in five hours at 120°. When decolorised with animal charcoal, the ester formed a pale brown, viscid liquid:

$$\begin{aligned} \alpha_D^{20} &= -20.89^\circ; \alpha_D^{100} = -13.41^\circ. \\ d_4^{20} &= 0.9947; d_4^{100} = 0.9363; l = 3.02 \text{ cm.} \\ [\alpha]_D^{20} &= -69.53^\circ; [\alpha]_D^{100} = -68.66^\circ. \\ [M]_D^{20} &= -240.6^\circ; [M]_D^{100} = -237.6^\circ. \end{aligned}$$

*Menthyl p-isoAmyloxybenzoate*.—Methyl *p*-isoamyloxybenzoate was obtained as a pale yellow oil, which distilled at 175—177°/13 mm. The acid crystallised in colourless needles, melting at 141—142°. The acid chloride, which was prepared by the direct action of phosphorus pentachloride on the acid, was a pale red liquid, which on distillation yielded a colourless liquid, boiling at 180—182°/12 mm. The action with menthol began at 105°, and was completed at 120°. The menthyl ester is a solid, which, after crystallisation from methyl alcohol, forms colourless needles, melting at 54—55°:

$\alpha_D^{20} - 21.51^\circ$ ;  $\alpha_D^{100} - 19.18^\circ$ .  
 $d_4^{20} = 0.9954$ ;  $d_4^{100} 0.9400$ ;  $l = 3.02$  cm.  
 $[\alpha]_D^{20} - 71.57^\circ$ ;  $[\alpha]_D^{100} - 67.57^\circ$ .  
 $[\text{M}]_D^{20} - 247.6^\circ$ ;  $[\text{M}]_D^{100} - 233.8^\circ$ .

*Menthyl o-Allyloxybenzoate*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_3\text{H}_5)\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ .—The methyl allyloxy-ester distilled at  $163^\circ/20$  mm. The acid crystallised from dilute alcohol in shining leaflets, melting at  $60\text{--}62^\circ$ . The acid chloride was prepared in benzene solution, and was obtained as a dark brown liquid which could not be distilled without decomposition. The action with menthol began at  $57^\circ$ . The resulting ester, which was dark red, was completely decolorised by animal charcoal. After recrystallisation from alcohol, it formed colourless, glistening leaflets, melting at  $61\text{--}62^\circ$ :

$\alpha_D^{100} - 16.19^\circ$ .  $d_4^{100} = 0.9689$ ;  $l = 3.02$  cm.  
 $[\alpha]_D^{100} - 55.35^\circ$ ;  $[\text{M}]_D^{100} - 174.9^\circ$ .

*Menthyl p-Allyloxybenzoate*.—The methyl allyloxy-ester distilled at  $163^\circ/15$  mm. It was hydrolysed with aqueous sodium hydroxide, and yielded an acid, which crystallised in leaflets, melting at  $160\text{--}162^\circ$ . To prepare the acid chloride, the acid was suspended in benzene, and phosphorus pentachloride added. The acid chloride dissolved, and, after removal of benzene and phosphoryl chloride, remained as a slightly discoloured liquid, which could not be distilled. The reaction with menthol began at  $85^\circ$ . The menthyl ester is a colourless, viscid liquid:

$\alpha_D^{20} - 24.71^\circ$ ;  $\alpha_D^{100} - 21.93^\circ$ .  
 $d_4^{20} = 1.027$ ;  $d_4^{100} = 0.9689$ ;  $l = 3.03$  cm.  
 $[\alpha]_D^{20} - 79.69^\circ$ ;  $[\alpha]_D^{100} - 74.95^\circ$ .  
 $[\text{M}]_D^{20} - 251.8^\circ$ ;  $[\text{M}]_D^{100} - 236.9^\circ$ .

*Menthyl o-Benzoyloxybenzoate*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_7\text{H}_7)\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$ .—Thirty-one grams of methyl salicylate were heated on the water-bath with 4.6 grams of sodium dissolved in 100 c.c. of methyl alcohol, and 25 grams of benzyl chloride for eight hours. To prevent humping and also to improve the yield, the bulk of the methyl alcohol was first removed by distilling from the water-bath. The product was shaken with sodium hydroxide solution to remove salicylic ester, and fractionated to separate benzyl chloride. Thirty-eight grams of ester were obtained, boiling at  $215\text{--}217^\circ/15$  mm. It solidified, on cooling, in large, colourless, prismatic crystals, melting at  $46\text{--}47^\circ$ . After hydrolysis with 20 per cent. sodium hydroxide solution, the liquid was extracted with ether to remove impurities, and acidified. The acid is precipitated at first as an oil, but soon solidifies, and, after crystallisation from methyl alcohol, melts at  $76\text{--}77^\circ$ . It was

treated in the usual way with phosphorus pentachloride, and the oxychloride removed. The product was a viscid, faintly brown liquid, which readily reacted with menthol, yielding a semisolid, transparent substance. In spite of various attempts to remove every trace of phosphoryl chloride from the acid chloride, the menthyl ester always contained an appreciable amount of phosphorus. Another preparation was therefore made with thionyl chloride in place of phosphorus chloride, which is probably purer and has a higher rotation. In the table on p. 1735 we have given the mean of the two results.

I.  $(\text{PCl}_5)$ :  $\alpha_D^{20} - 15.55^\circ$ ;  $\alpha_D^{100} - 13.90^\circ$ .

II.  $(\text{SOCl}_2)$ :  $\alpha_D^{20} - 16.23^\circ$ ;  $\alpha_D^{100} - 14.55^\circ$ .

I.  $d_4^{20} = 1.147$ ;  $d_4^{100} = 1.089$ ;  $l = 3.02$  cm.

II.  $d_4^{20} = 1.142$ ;  $d_4^{100} = 1.083$ ;  $l = 3.02$  cm.

I.  $[\alpha]_D^{20} - 44.89^\circ$ ;  $[\alpha]_D^{100} - 42.28^\circ$ .

II.  $[\alpha]_D^{20} - 47.07^\circ$ ;  $[\alpha]_D^{100} - 44.49^\circ$ .

I.  $[\text{M}]_D^{20} - 164.3^\circ$ ;  $[\text{M}]_D^{100} - 154.7^\circ$ .

II.  $[\text{M}]_D^{20} - 172.3^\circ$ ;  $[\text{M}]_D^{100} - 162.8^\circ$ .

*Menthyl p-Benzoyloxybenzoate*.—The methyl benzyloxy-ester was prepared like the previous compound, and melted at  $99^\circ$ . It was hydrolysed with 20 per cent. methyl-alcoholic potassium hydroxide solution. The potassium salt, which separated on cooling, was recrystallised from water, and gave an acid, which crystallised in colourless needles, and melted at  $188$ – $190^\circ$ . The acid was dissolved in four to five times its weight of benzene, and the phosphorus chloride added. On heating on the water-bath, the acid dissolved, and, on cooling, the acid chloride crystallised in colourless needles, melting at  $104$ – $106^\circ$ . It was washed with light petroleum, and heated with menthol. The action began about  $100^\circ$ , and was completed in two hours at  $140^\circ$ . The substance, which remained liquid for some time, slowly crystallised:

$\alpha_D^{20} - 22.40^\circ$ ;  $\alpha_D^{100} - 19.75^\circ$ .

$d_4^{20} = 1.064$ ;  $d_4^{100} = 1.0015$ ;  $l = 3.02$  cm.

$[\alpha]_D^{20} - 69.68^\circ$ ;  $[\alpha]_D^{100} - 65.29^\circ$ .

$[\text{M}]_D^{20} - 255.1^\circ$ ;  $[\text{M}]_D^{100} - 238.9^\circ$ .

*Menthyl o-Dimethylaminobenzoate*,  $\text{C}_6\text{H}_4(\text{NMe}_2) \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_{19}$ .—The *o*-dimethylamino acid was obtained from anthranilic acid and methyl sulphate by Willstätter and Kahn's method (*Ber.*, 1904, 37, 406). The anthranilic acid is first converted into monomethylaminobenzoic acid (m. p.  $177^\circ$ ), then into the methyl ester, which distils at  $134$ – $135^\circ/14$  mm., and solidifies on cooling (m. p. about  $15$ – $16^\circ$ ). This is converted into the dimethylamino-ester, and finally by boiling with water into the acid. The acid when re-

crystallised from ether melts at  $72^{\circ}$ , and not at  $70^{\circ}$  as given by the authors. The acid was heated on the water-bath with three times its weight of thionyl chloride, and the excess removed in a current of dry air under diminished pressure. The residue, which had an orange colour, was mixed with menthol and heated to  $100^{\circ}$ . On shaking, a vigorous action began with evolution of hydrogen chloride, and was completed at  $120^{\circ}$ . The product was a dark red mass, from which some of the colour was removed after keeping for several days in ethereal solution with animal charcoal. It was dissolved in light petroleum, and precipitated by dry hydrogen chloride as the hydrochloride in the form of a viscid liquid. This was separated and converted into the ester without, however, any change of colour. The product gave a correct analysis, and therefore we are disposed to regard the substance as moderately pure:

$$\alpha_D^{100} - 10.24^{\circ}; \quad d_4^{100} = 1.019; \quad l = 3.02 \text{ cm.}$$

$$[\alpha]_D^{100} - 33.29^{\circ}; \quad [M]_D^{100} - 100.9^{\circ}.$$

*Methyl p-Dimethylaminobenzoate.*—*p*-Aminobenzoic acid was converted into the dimethylamino-acid by Willstätter and Kahn's method (*loc. cit.*), and melted at  $235^{\circ}$ . It was heated with three times its weight of thionyl chloride, and, on removal of the excess of the latter, the acid chloride solidified as an orange, crystalline mass. A portion of this was warmed with methyl alcohol, and after removal of the alcohol gave a crystalline ester, which had the correct melting point ( $102^{\circ}$ ). It may be assumed therefore that the acid chloride was moderately pure. It was heated with menthol to  $120^{\circ}$ , and the product purified in the usual way. The ester is precipitated as hydrochloride from its solution in light petroleum, but has the same red colour as the ortho-compound both before and after precipitation, and gave nearly the same rotation number:

	Before precipitation.	After precipitation.
$\alpha_D^{100}$ .....	$-25.56^{\circ}$	$-25.33^{\circ}$

$$d_4^{100} = 0.9852; \quad l = 3.02 \text{ cm.}$$

$$[\alpha]_D^{100} - 85.13^{\circ}; \quad [M]_D^{100} - 257.9^{\circ}.$$

*Methyl  $\alpha$ -Methoxynaphthoate*,  $C_{10}H_6(OMe) \cdot CO_2 \cdot C_{10}H_7$ .—The methyl ester was obtained by the action of methyl iodide on the silver salt of  $\alpha$ -hydroxynaphthoic acid. It forms red, prismatic crystals, which, on recrystallisation from alcohol with the addition of charcoal, become colourless, and melt at  $74$ – $76^{\circ}$ . The methoxy-ester is a dark red oil, which became pale yellow on distillation, and boiled at  $193$ – $195^{\circ}/17 \text{ mm.}$  It was hydrolysed with 20 per cent. sodium hydroxide solution. The addition of alkali immediately produced a red colour, and this red colour was also observed

in the different alkaline salts of the original hydroxynaphthoic acid. The methoxy-acid, on recrystallisation from alcohol, gave colourless needles, melting at 120–123°. The acid chloride, which was prepared by the action of phosphorus pentachloride in benzene solution, crystallises in fine, colourless needles. The reaction with menthol began at 87°, and was completed at 120° in five and a-half hours. The ester is a very viscid, pale yellow substance:

$$\begin{aligned} \alpha_D^{20} &= -25.43^\circ; \alpha_D^{100} = -21.69^\circ. \\ d_4^{20} &= 1.076; d_4^{100} = 1.022; l = 3.02 \text{ cm.} \\ [\alpha]_D^{20} &= -78.27^\circ; [\alpha]_D^{100} = -70.32^\circ. \\ [M]_D^{20} &= -266.2^\circ; [M]_D^{100} = -239.0. \end{aligned}$$

*Menthyl  $\beta$ -Methoxynaphthoate.*— $\beta$ -Hydroxynaphthoic acid was converted into the methyl ester by boiling 50 grams with 200 c.c. of methyl alcohol and 10 c.c. of concentrated sulphuric acid. It yielded 46 grams of crude ester, which, after crystallisation from alcohol, consisted of pale yellow needles (m. p. 73–74°). This was converted in the usual way into the methoxy-ester, boiling at 217°/20 mm. It solidified, on cooling, in massive plates (m. p. 45–47°). It was hydrolysed in the ordinary way, and the acid, when crystallised from alcohol, melted at 126–130°. It was converted into the acid chloride by heating with an equal weight of phosphorus pentachloride, and, when freed from oxychloride, crystallised. The action with menthol began on warming gently. The menthyl ester solidified; it melts at 88.5–90°:

$$\begin{aligned} \alpha_D^{20} &= -16.20^\circ; \alpha_D^{100} = -14.50^\circ. \\ d_4^{20} &= 1.083; d_4^{100} = 1.025; l = 3.02 \text{ cm.} \\ [\alpha]_D^{20} &= -48.94^\circ; [\alpha]_D^{100} = -46.84^\circ. \\ [M]_D^{20} &= -166.4^\circ; [M]_D^{100} = -159.2^\circ. \end{aligned}$$

*Menthyl  $\beta$ -Benzoxynaphthoate,*  $C_{10}H_6(O \cdot C_6H_5) \cdot CO_2 \cdot C_{10}H_{19}$ .—The methyl ester was obtained by acting on the sodium compound of  $\beta$ -hydroxynaphthoic ester with benzyl chloride, and formed a dark red, viscid liquid, which could not be distilled. It was hydrolysed with 20 per cent. alcoholic potash. The acid was precipitated as a sticky mass, which solidified on keeping, and crystallised from alcohol in colourless needles, melting at 130–132°. The acid chloride was obtained as a hard, transparent, yellow mass by the action of phosphorus pentachloride in benzene solution. The menthyl ester was prepared by heating the acid chloride with menthol to 120° for six and a-half hours. The reaction began at 85°. The menthyl ester is a brown, transparent solid, which is very viscid at 100°:

$$\begin{aligned} \alpha_D^{20} &= -29.46^\circ; \alpha_D^{100} = -24.87^\circ. \\ d_4^{20} &= 1.118; d_4^{100} = 1.058; l = 3.02 \text{ cm.} \end{aligned}$$

$$[\alpha]_D^{25} - 87.27^\circ; [\alpha]_D^{100} - 77.82^\circ.$$

$$[M]_D^{25} - 363.0^\circ; [M]_D^{100} - 324.4^\circ.$$

*Menthyl o-Toluate*,  $C_6H_4Me \cdot CO_2 \cdot C_{10}H_{19}$ .—The acid chloride, prepared by the action of phosphorus pentachloride on the acid, is a colourless liquid (b. p. 99–103°/11 mm.). The action with menthol began at 68°. The menthyl ester is a colourless, viscid liquid, which distils at 213–215°/25 mm.:

	Undistilled.	Distilled.
$\alpha_D^{25}$ .....	-25.45°	-25.43°
$\alpha_D^{100}$ .....	23.05	23.07

$$d_4^{25} = 0.9982; d_4^{100} = 0.9383; l = 3.02 \text{ cm.}$$

$$[\alpha]_D^{25} - 84.35^\circ; [\alpha]_D^{100} - 81.41^\circ.$$

$$[M]_D^{25} - 231.1^\circ; [M]_D^{100} - 223.1^\circ.$$

*Menthyl m-toluate* was prepared as above. The acid chloride is a colourless liquid, boiling at 136–138°/31 mm. The reaction with menthol began at 97°. The menthyl ester is a colourless, rather viscid liquid, boiling at 228–229°/36 mm.:

	Undistilled.	Distilled.
$\alpha_D^{25}$ .....	-26.47°	-23.31°
$\alpha_D^{100}$ .....	24.29	24.18

$$d_4^{25} = 0.9946; d_4^{100} = 0.9352; l = 3.02 \text{ cm.}$$

$$[\alpha]_D^{25} - 87.59^\circ; [\alpha]_D^{100} - 85.63^\circ.$$

$$[M]_D^{25} - 247.0^\circ; [M]_D^{100} - 234.7^\circ.$$

*Menthyl p-toluate* was prepared as above. The acid chloride is a colourless liquid. The reaction with menthol began at 78°. The menthyl ester is a colourless, crystalline substance, boiling at 196–198°/11 mm., and melting at 40–41°:

	Undistilled.	Distilled.
$\alpha_D^{25}$ .....	-27.02°	-26.99°
$\alpha_D^{100}$ .....	24.36	24.40

$$d_4^{25} = 0.9937; d_4^{100} = 0.9336; l = 3.02 \text{ cm.}$$

$$[\alpha]_D^{25} - 89.93^\circ; [\alpha]_D^{100} - 86.56^\circ.$$

$$[M]_D^{25} - 246.4^\circ; [M]_D^{100} - 237.2^\circ.$$

*Menthyl Phenylacetate*,  $C_6H_5 \cdot CH_2 \cdot CO_2 \cdot C_{10}H_{19}$ .—The action of menthol on phenylacetyl chloride began at 50°. The ester is a colourless, mobile liquid, boiling at 192–197°/10 mm.:

	Undistilled.	Distilled.
$\alpha_D^{25}$ .....	-20.85°	-20.79°
$\alpha_D^{100}$ .....	13.74	13.61

$$d_4^{25} = 1.002; d_4^{100} = 0.9400; l = 3.02 \text{ cm.}$$

$$[\alpha]_D^{25} - 68.70^\circ; [\alpha]_D^{100} - 65.56^\circ.$$

$$[M]_D^{25} - 188.2^\circ; [M]_D^{100} - 179.6^\circ.$$



*Menthyl benzoate*,  $C_6H_5 \cdot CO_2 \cdot C_{10}H_{19}$ , was obtained by the action of menthol on benzoyl chloride, which began at  $88^\circ$ . The ester is a colourless, crystalline solid, melting at  $54^\circ$ . In order to determine the rotation and density at  $20^\circ$ , the rotation at  $100^\circ$  was first determined, and the liquid allowed to cool somewhat, when a current of water at  $20^\circ$  was allowed to run through the jacket of the polarimeter tube for some time. As soon as the first indications of crystallisation appeared, a reading was taken, and the process repeated. The density was first taken in the pyknometer at  $100^\circ$ , and then the liquid supercooled in water at  $20^\circ$ . As crystallisation always commenced at the ends of the limbs, it was found that by keeping the ends warm by touching them occasionally with the tip of a Bunsen flame, crystallisation could be prevented for any length of time:

$$\begin{aligned} \alpha_D^{20} &= -27.83^\circ; \alpha_D^{100} = -25.45^\circ. \\ d_4^{20} &= 1.002; d_4^{100} = 0.9417; l = 3.02 \text{ cm.} \\ [\alpha]_D^{20} &= -19.95^\circ; [\alpha]_D^{100} = -89.47^\circ. \\ [M]_D^{20} &= -239.0^\circ; [M]_D^{100} = -232.7^\circ. \end{aligned}$$

The following table contains the analytical results:

Ester.	Substance taken.	CO <sub>2</sub> .	H <sub>2</sub> O.	C found.	C calc.	H found.	H calc.
<i>o</i> -Methoxybenzoic ester.....	0.1409	0.3855	0.1149	74.64	74.48	9.05	8.96
<i>m</i> -Methoxybenzoic „ .....	0.1364	0.3721	0.1083	74.39		8.82	
<i>p</i> -Methoxybenzoic „ .....	0.1542	0.4200	0.1248	74.27	74.56	8.99	9.24
<i>o</i> -Ethoxybenzoic „ .....	0.1423	0.3874	0.1184	74.27		9.17	
<i>m</i> -Ethoxybenzoic „ .....	0.1432	0.3921	0.1197	74.68	75.50	9.30	9.40
<i>p</i> -Ethoxybenzoic „ .....	0.1544	0.4216	0.1295	74.47		9.32	
<i>o</i> -Propoxybenzoic „ .....	0.1641	0.4539	0.1385	75.50	75.50	9.37	9.53
<i>m</i> -Propoxybenzoic „ .....	0.1645	0.4558	0.1410	75.60		9.50	
<i>p</i> -Propoxybenzoic „ .....	0.1551	0.4289	0.1330	75.44	76.30	9.29	9.50
<i>o</i> -isoPropoxybenzoic ester...	0.1680	0.4560	0.1404	74.10		9.29	
<i>p</i> -isoPropoxybenzoic „ .....	0.1674	0.4616	0.1412	75.20	76.30	9.37	9.50
<i>o</i> -isoAmyloxybenzoic „ .....	0.1618	0.4508	0.1431	76.0		9.33	
<i>m</i> -isoAmyloxybenzoic „ .....	0.1550	0.4280	0.1374	75.43	76.0	9.35	9.50
<i>p</i> -isoAmyloxybenzoic „ .....	0.1432	0.3982	0.1265	75.90		9.31	
<i>o</i> -Allyloxybenzoic „ .....	0.1587	0.4410	0.1274	75.80	78.70	8.92	8.9
<i>p</i> -Allyloxybenzoic „ .....	0.1589	0.4414	0.1261	75.80		8.92	
<i>o</i> -Benzyloxybenzoic „ .....	0.1612	0.4620	0.1061	78.20	77.70	7.32	8.20
<i>p</i> -Benzyloxybenzoic „ .....	0.1618	0.4653	0.1231	78.59		8.45	
<i>a</i> -Methoxynaphthoic „ .....	0.1639	0.4655	0.1221	77.55	80.76	8.27	8.20
<i>B</i> -Methoxynaphthoic „ .....	0.1357	0.3865	0.1008	77.67		8.25	
<i>B</i> -Benzyloxynaphthoic ester	0.1649	0.4849	0.1132	80.29		7.62	7.09

*o*-Dimethylaminobenzoic ester: 0.2264 gave 9.5 c.c. N<sub>2</sub> (moist) at  $19^\circ$  and 752 mm. N=4.80. Calc., N=4.90 per cent.

*p*-Dimethylaminobenzoic ester: 0.2105 gave 8.3 c.c. N<sub>2</sub> (moist) at  $21^\circ$  and 744 mm. N=4.52. Calc., N=4.90 per cent.

We gratefully acknowledge the help of Mr. C. E. C. Ferry in

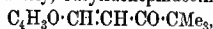
the preparation of the three ethoxybenzoic esters. We also desire to thank the Research Fund Committee of the Chemical Society for funds which have defrayed the greater part of the cost of the materials used in the above investigation.

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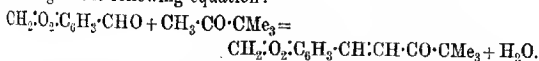
CLXXXV.—*A Study of Some Unsaturated Compounds  
Containing the tert.-Butyryl Group. Part I.*

By ALFRED ARCHIBALD BOON and FORSYTH JAMES WILSON.

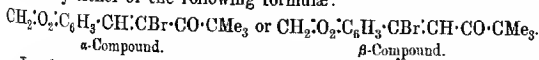
ONE of us has recently shown that the action of phosphorus pentasulphide on desylpinacoline appears to be abnormal (this vol., p. 1257). With the view of investigating the action of organic compounds of sulphur on substances containing the *tert.*-butyryl group, we intend studying some of the ketones having the general formula  $R \cdot CH:CH \cdot CO \cdot CMe_3$ , where R is invariably an aryl radicle. Some years ago a number of such compounds, which are related to benzylidenepinacoline (*Ber.*, 1897, **30**, 2268), were prepared by us. One of these, namely, furylidenepinacoline,



a pale yellow, oily liquid with a very characteristic odour, was found to be vigorously attacked by bromine with apparent decomposition; so we were induced to try the action of bromine on some of our other preparations. The results of our investigation on piperonylidenepinacoline form the subject of this communication. By means of aqueous sodium hydroxide, piperonal can be condensed with pinacoline in alcoholic solution, with the formation of *piperonylidenepinacoline* ( $\alpha$ -*tert.*-butyryl- $\beta$ -piperonylethylene), according to the following equation:



This compound melts at 94–95°, and is attacked by bromine at the ordinary temperature, forming chiefly piperonylidenepinacoline dibromide,  $CH_2:O_2 \cdot C_6H_3 \cdot CHBr \cdot CHBr \cdot CO \cdot CMe_3$  (m. p. 138–139°), and also, to a small extent, another substance, which apparently is a monobromo-compound (m. p. 110–111°), and may be represented by either of the following formulæ:



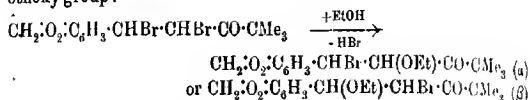
$\alpha$ -Compound.

$\beta$ -Compound.

In brominating piperonylidenepinacoline, we tried various solvents. Chloroform was found to be the best, glacial acetic acid

suitable, but carbon disulphide of very little value, very poor yields being obtained in this case.

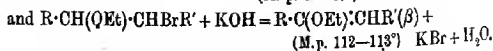
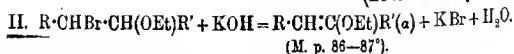
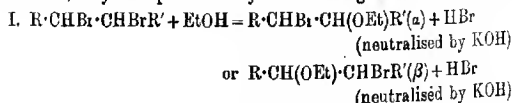
When piperonylidenepinacoline dibromide was boiled with absolute alcohol, after a time it was found that the latter gave an acid reaction, and a compound was ultimately obtained which still contained bromine. These facts, coupled with our analysis of the substance, appeared to show that one of the bromine atoms of piperonylidenepinacoline dibromide had been replaced by an ethoxy-group:



This compound melts at 82–83°, and was found to be identical with that produced by boiling piperonylidenepinacoline dibromide with one molecular proportion of potassium hydroxide in alcoholic solution, the above reaction no doubt taking place, but the hydrobromic acid in this case being neutralised by the alkali present. When, however, piperonylidenepinacoline dibromide was treated with two molecular proportions of potassium hydroxide in alcoholic solution, three compounds were obtained. One of these, which constituted the chief product of the reaction, was *ethoxy-piperonylidenepinacoline*, which we have provisionally formulated as the  $\beta$ -compound,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:C(OEt):CH-CO-CMe}_3$  (m. p. 112–113°).

The other compounds were: a substance having the same composition as the  $\beta$ -compound and probably isomeric with it ( $\alpha$ -compound) (m. p. 86–87°), and also a substance containing bromine, which appeared to be identical with the ethoxy-derivative ( $\alpha$  or  $\beta$ ) (m. p. 82–83°) already referred to.

The latter substance seems therefore to be the initial product of the reaction, and hence the possible changes involved in the formation of the compounds, obtained when an alcoholic solution of potassium hydroxide is allowed to act on piperonylidenepinacoline dibromide, may be represented by the following scheme:



where R and R' represent respectively  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:}$  and  $\text{-CO-CMe}_3$ .

These ethoxy-compounds may, however, be stereoisomerides, and it is interesting to note that they are analogues of the ethyl ether of dibenzoylmethane obtained by Ruhemann and Watson in their critical study of Wislicenus's isomeride of dibenzoylmethane (Trans., 1904, 85, 456). Piperonylidenepinacoline, when acted on by hydroxylamine hydrochloride at the ordinary temperature, yields an *azime* (m. p. 144—145°).

#### EXPERIMENTAL.

*Piperonylidenepinacoline* ( $\alpha$ -tert.-Butyryl- $\beta$ -piperonylethylene),  
 $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH:CH:CO-CMe}_3$ .

To a solution containing 90 grams of piperonal and 64 grams of pinacoline in 450 c.c. of absolute alcohol, 100 c.c. of a 10 per cent. solution of sodium hydroxide were added. This mixture was heated for ten minutes on a water-bath, and then kept for twenty-four hours at the ordinary temperature.

The crystalline mass thus obtained was collected, and to the filtrate 50 c.c. of a 20 per cent. solution of sodium hydroxide were added. After keeping for a day, a crystalline precipitate was again obtained; this was collected, and the filtrate, to which 25 c.c. of a 20 per cent. solution of sodium hydroxide were added, was kept for two days. A further yield of the crude crystalline product was thus collected, and the filtrate precipitated with water. The various crops of the crude mother substance obtained in these operations were purified by crystallisation from boiling alcohol. The yield was extremely good:

0.1824 gave 0.4823  $\text{CO}_2$  and 0.1141  $\text{H}_2\text{O}$ .  $\text{C}=72.11$ ;  $\text{H}=6.95$ .

0.1891 „ 0.5007  $\text{CO}_2$  „ 0.1179  $\text{H}_2\text{O}$ .  $\text{C}=72.21$ ;  $\text{H}=6.93$ .

0.1993, in 48.15 of nitrobenzene, gave  $\Delta t = -0.127^\circ$ . M.W. = 228.

$\text{C}_{14}\text{H}_{16}\text{O}_3$  requires  $\text{C}=72.41$ ;  $\text{H}=6.89$  per cent. M.W. = 232.

*Piperonylidenepinacoline* melts at 94—95°. When crystallised from absolute alcohol, it is obtained in pale yellow needles. It is very soluble in benzene or chloroform, but less so in light petroleum.

#### Action of Bromine on Piperonylidenepinacoline.

As stated in the introduction, chloroform was found to be the best solvent in this reaction. Piperonylidenepinacoline was dissolved in dry chloroform, the calculated quantity of dry bromine (2 mols.), dissolved in dry chloroform, was gradually added, and the solvent afterwards removed by a current of dry air. The residue was then fractionally crystallised from glacial acetic acid. A very good yield (75 per cent.) of *piperonylidenepinacoline dibromide*,

$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CMe}_3$ , which was the main product, was thus obtained:

0.2548 gave 0.2458 AgBr. Br=41.02.

0.1171 „ 0.1124 AgBr. Br=40.93.

$\text{C}_{14}\text{H}_{16}\text{O}_3\text{Br}_2$  requires Br=40.81 per cent.

*Piperonylidenepinacoline dibromide* melts at 138–139°, and can be obtained in colourless needles from light petroleum, in which it is sparingly soluble. It dissolves readily in benzene, but less so in acetic acid. In this reaction, to a small extent, another substance was obtained in short, colourless prisms from light petroleum. It was found to be more soluble in acetic acid (and the other solvents mentioned above) than the dibromide, and appears to be a *monobromide* of *piperonylidenepinacoline*:

$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{CBr}\cdot\text{CO}\cdot\text{CMe}_3$ ,  $\alpha$ -compound, or

$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_5\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}_3$ ,  $\beta$ -compound.

This substance melts at 110–111°, and is apparently unsaturated, as it combines with bromine in chloroform solution:

0.1659 was found equivalent to 5.15 c.c.  $N/10\text{-AgNO}_3$ . Br=24.83.

$\text{C}_{14}\text{H}_{15}\text{O}_3\text{Br}$  requires Br=25.72 per cent.

A number of analyses were made of this compound, but in every case the result obtained was low.

*Action of Ethyl Alcohol on Piperonylidenepinacoline Dibromide:  
Formation of Bromoethoxypiperonylidenepinacoline.*

$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CH}(\text{OEt})\cdot\text{CO}\cdot\text{CMe}_3$ ,  $\alpha$ -compound, or

$\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_5\cdot\text{CH}(\text{OEt})\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CMe}_3$ ,  $\beta$ -compound.

Piperonylidenepinacoline dihydromide was boiled with absolute alcohol, in which it gradually dissolved, the solution giving an acid reaction. After about four hours' boiling, the solution, on cooling, deposited fine, colourless needles, which were collected and recrystallised from boiling alcohol. As mentioned above, in this reaction an atom of bromine in the dihydromide is apparently replaced by an ethoxy-group:

0.1474 was found equivalent to 4.10 c.c.  $N/10\text{-AgNO}_3$ . Br=22.25.

$\text{C}_{16}\text{H}_{21}\text{O}_4\text{Br}$  requires Br=22.40 per cent.

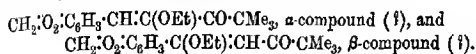
*Bromoethoxypiperonylidenepinacoline* melts at 82–83°, and can also be obtained by the action of one molecule of potassium hydroxide on an alcoholic solution of piperonylidenepinacoline dihydromide. An estimation of the bromine contained in the compound obtained by this method gave the following result:

0.1850 was found equivalent to 5.20 c.c.  $N/10\text{-AgNO}_3$ . Br=22.49.

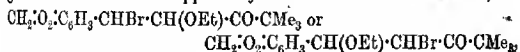
$\text{C}_{16}\text{H}_{21}\text{O}_4\text{Br}$  requires Br=22.40 per cent.

(The average result of a number of analyses, made with samples obtained by both methods of production, gave Br=22.12 per cent.)

*Action of Potassium Hydroxide (2 mols.) on Piperonylidene-pinacolone Dibromide in Alcoholic Solution: Formation of Ethoxypiperonylidene-pinacolone ( $\alpha$  and  $\beta$ ).*



Piperonylidene-pinacolone dibromide was dissolved in hot alcohol, and the necessary quantity (2 mols.) of potassium hydroxide dissolved in absolute alcohol added; potassium bromide was at once precipitated, and, to complete the action, the mixture was warmed for one hour on the water-bath. The solution, after being filtered, was evaporated, and the residue extracted with ether to remove potassium bromide. The ethereal solution was next evaporated, and the residue recrystallised from light petroleum. In this way there was obtained a colourless, crystalline substance, which, after recrystallisation from alcohol, and then from a mixture of benzene and light petroleum, melted at 112–113°. This constituted the main product of the reaction. From the mother liquor there was obtained—in small amount only—a colourless, crystalline substance, which, after recrystallisation from alcohol, melted at 86–87°. The light petroleum mother liquors, on evaporation, gave a large quantity of oil, which, after some time, partly solidified, giving a further yield of the main product (m. p. 112–113°), whilst the residual oil, on cooling and long keeping, solidified to some extent, and yielded a substance melting at 82–83°, which in its general behaviour was apparently identical with the substance,



already mentioned.

The analytical results for the substances melting at 112–113° and 86–87° are as follows:

Substance melting at 112–113°.

0.1122 gave 0.2857 CO<sub>2</sub> and 0.0750 H<sub>2</sub>O. C=69.43; H=7.48.  
 0.1195 „ 0.3044 CO<sub>2</sub> „ 0.0782 H<sub>2</sub>O. C=69.46; H=7.28.  
 0.3010, in 25.33 of nitrobenzene, gave  $\Delta t = -0.290^\circ$ . M.W.=285.  
 C<sub>16</sub>H<sub>20</sub>O<sub>4</sub> requires C=69.56; H=7.24 per cent. M.W.=276.

Substance melting at 86–87°.

0.1382 gave 0.3552 CO<sub>2</sub> and 0.0907 H<sub>2</sub>O. C=70.09; H=7.29.  
 C<sub>16</sub>H<sub>20</sub>O<sub>4</sub> requires C=69.56; H=7.24 per cent.

*Action of Hydroxylamine on Piperonylidene-pinacoline.*

Piperonylidene-pinacoline yields an *oxime*,  $C_{14}H_{17}O_3N$ . This was prepared by the action of 2.08 grams of  $\alpha$ -hydroxylamine hydrochloride on 2.32 grams of the ketone in presence of 3 grams of potassium acetate. The oxime was precipitated by the addition of water, and purified by recrystallisation from alcohol. It is a colourless, crystalline substance, melting at  $144-145^\circ$ :

0.1880 gave 9.8 c.c.  $N_2$  (moist) at  $16.6^\circ$  and 741 mm.  $N=5.92$ .

0.1630 „ 8.5 c.c.  $N_2$  (moist) „  $21.6^\circ$  „ 767 mm.  $N=5.94$ .

$C_{14}H_{17}O_3N$  requires  $N=5.67$  per cent.

We are continuing this investigation, more particularly with the object of obtaining some knowledge of the constitution of the ethoxy-derivatives mentioned above, and of extending our work to substances having the general formula  $R\cdot CH:CH\cdot CO\cdot CMe_2$  referred to in the introduction.

CHEMICAL LABORATORIES,  
HERRIOT WATT COLLEGE, EDINBURGH,

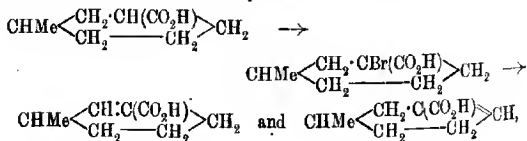
AND

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE, GLASGOW.

CLXXXVI.—*Carboxylic Acids of cycloHexanone and some of its Derivatives.*

By HENRY DENT GARDNER, WILLIAM HENRY PERKIN, jun., and  
HUBERT WATSON.

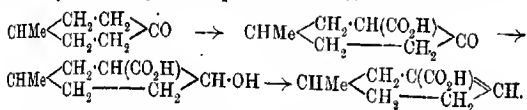
THE present investigation had for its principal object an attempt to devise a method by which certain unsaturated acids, required for synthetical experiments in the terpene group, could be obtained in quantity sufficient for that purpose. It has, for example, already been shown (Perkin and Tattersall, *Trans.*, 1905, **87**, 1085) that *m*-toluic acid is converted by reduction and subsequent bromination and elimination of hydrogen bromide into a mixture of 1-methyl- $\Delta^1$ - and  $\Delta^3$ -cyclohexene 3 carboxylic acids:



but the process, involving, as it does, reduction with sodium and isomyl alcohol, is an unpleasant and tedious one, and, furthermore, the isomeric acids are difficult to separate. Consequently, the terpeneols and terpenes obtained from these acids could not be investigated in so thorough a manner as was desirable.

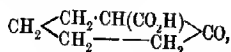
Now, it seemed possible that a more convenient method of preparation of 1-methyl- $\Delta^3$ -cyclohexene-3-carboxylic acid might result from the following series of decompositions.

1-Methylcyclohexan-4-one, which is now readily obtained in quantity from *p*-cresol by the Sabatier-Sendrens process, might be readily converted into 1-methylcyclohexan-4-one-3-carboxylic acid by the action of sodamide and carbon dioxide, and this acid, on reduction, should yield 1-methylcyclohexan-4-ol-3-carboxylic acid, from which by the elimination of water, 1-methyl- $\Delta^3$ -cyclohexene-3-carboxylic acid might be expected to result:



In a later communication it will be shown that this unsaturated acid may, in fact, be conveniently prepared by this process, and in quantity sufficient to allow of the complete characterisation of the terpeneol and terpene derived from it. It has also been found possible to prepare sufficient of this acid to allow of its resolution by means of the brucine salt, and the preparation and examination of the active terpeneols and terpenes derived from the *d*- and *l*-acids thus obtained is in active progress. There can be no doubt that other unsaturated acids of this kind will result from a similar series of reactions carried out with the aid of suitable derivatives of cyclohexanone. The action of sodium or sodamide and carbon dioxide on cyclic ketones does not appear to have been investigated, and the present communication deals with the conditions under which such action takes place, and with the reduction of the resulting ketonic acids to the corresponding hydroxy-acids.

Because it is the cyclic ketone that is most readily obtained in a pure condition, the first experiments were made with cyclohexanone itself, and it was found that this ketone is converted into cyclohexanone-2-carboxylic acid:

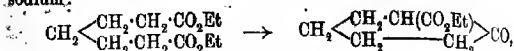


when its solution in ether is treated first with sodamide and then with carbon dioxide.

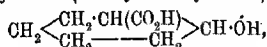
The ester of this acid had already been prepared by Dieckmann.



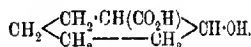
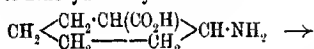
(*Annalen*, 1901, 317, 93) from ethyl pimelate by the action of sodium:



but, owing to its instability, it was not found possible to obtain the free acid by the hydrolysis of this ester. *cyclo*Hexanone-2-carboxylic acid melts and decomposes at 81–82°, and gives an intense purple coloration when ferric chloride is added to its aqueous solution. It is readily reduced by sodium amalgam to *cyclo*hexanol-2-carboxylic acid (hexahydrosalicylic acid):

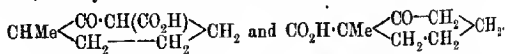


which melts at 111°, and had already been obtained by Dieckmann (*Ber.*, 1894, 27, 2745) from ethyl *cyclo*hexanone-2-carboxylate by reduction with sodium amalgam and water. It is well known that, when salicylic acid is reduced in *iso*amyl-alcoholic solution with sodium, it does not yield hexahydrosalicylic acid, but that fission of the ring occurs, and the product is pimelic acid. Einhorn and Meyenberg (*Ber.*, 1894, 27, 2466), however, showed that anthranilic acid may be reduced to hexahydroanthranilic acid, and that this acid, when treated with nitrous acid, is decomposed with formation of hexahydrosalicylic acid:



We next experimented on the action of sodamide and carbon dioxide on 1-methyl*cyclo*hexan-2-one, and obtained 1-methyl*cyclo*hexan-2-one-3-carboxylic acid, and from this, by reduction with sodium amalgam, we prepared 1-methyl*cyclo*hexan-2-ol-3-carboxylic acid.

With regard to the constitution of the keto-acid, it is clear that there are two isomerides which might conceivably be produced by the action of sodamide and carbon dioxide on 1-methyl*cyclo*hexan-2-one, namely:

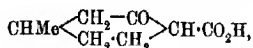


1-Methyl*cyclo*hexan-2-one-3-carboxylic acid.

1-Methyl*cyclo*hexan-2-one-1-carboxylic acid.

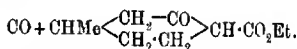
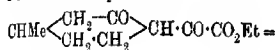
Since, however, the acid actually produced gives an intense coloration with ferric chloride, it cannot be 1-methyl*cyclo*hexan-2-one-1-carboxylic acid, and must therefore be 1-methyl*cyclo*hexan-2-one-3-carboxylic acid. More interesting results were obtained during the course of our experiments on the action of sodamide and

carbon dioxide on 1-methylcyclohexan-3-one. We investigated, in the first place, the behaviour of the *dl*-ketone under these conditions, and found that it was comparatively readily converted into a keto-acid, which is probably *dl*-1-methylcyclohexan-3-one-4-carboxylic acid:



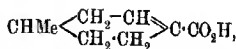
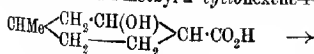
but in which the carboxyl group may possibly occupy the 2-position.

This acid melts at 100–103°, yields an ester distilling at 132–135°/24 mm., and is reduced by sodium amalgam to *dl*-1-methylcyclohexan-3-ol-4-carboxylic acid (m. p. 129–130°). Ethyl 1-methylcyclohexan-3-one-4-carboxylate had already been prepared by Kötze and Hesse (*Annalen*, 1905, 342, 310) from 1-methylcyclohexan-3-one by condensation with ethyl oxalate and subsequent distillation of the ethyl 1-methylcyclohexan-3-one-4-oxalate thus produced:



These investigators give 115°/12 mm. as the boiling point of this ester, and they were unable to obtain the free acid by hydrolysing it, because of the readiness with which it is decomposed into methylcyclohexanone and carbon dioxide.

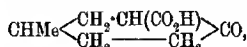
We next investigated the action of sodamide and carbon dioxide on *d*-1-methylcyclohexan-3-one from pulegone (Wallach, *Annalen*, 1896, 289, 339), and found that, under the conditions described in the experimental part of this paper, this ketone, of specific rotation  $[\alpha]_D + 8.8^\circ$ , is converted into *d*-1-methylcyclohexan-3-one-4-carboxylic acid, which melts at 102–103°, and has  $[\alpha]_D + 97.2^\circ$ , and the ethyl ester of which has  $[\alpha]_D + 84.16^\circ$ . When the *d*-keto-acid was reduced with sodium amalgam, it yielded a *d*-1-methylcyclohexan-3-ol-4-carboxylic acid, which melted at 129–130° and had  $[\alpha]_D - 31.8^\circ$ , the sign of rotation having changed during reduction. Probably direct or indirect elimination of water will convert this acid into *d*-1-methyl- $\Delta^3$ -cyclohexene-4-carboxylic acid:



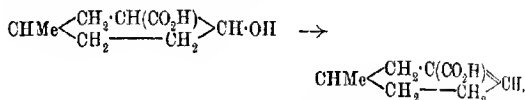
and this probability is being tested by experiment.

The investigation of the behaviour of 1-methylcyclohexan-4-one with sodamide and carbon dioxide seems to show that this ketone

reacts much more readily with this reagent than is the case with the cyclic ketones which have already been mentioned. Under conditions which have been carefully worked out (p. 1769), a yield of at least 40 per cent. of 1-methylcyclohexan-2-one-3-carboxylic acid:



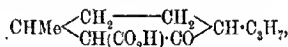
is quite easily obtained. This acid melts at  $101^\circ$ , and is converted, by reduction, into 1-methylcyclohexan-4-ol-3-carboxylic acid, which melts at  $114^\circ$ , and, on distillation under diminished pressure, is decomposed with elimination of water and formation of 1-methyl- $\Delta^3$ -cyclohexene-4-carboxylic acid:



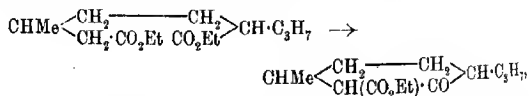
The description of the results which have been obtained during a long investigation of this acid and its derivatives is reserved for a future communication.

During the course of the experiments, which have been briefly summarised in the preceding pages, it appeared to us that it would be interesting to include *l*-menthone in the scope of this investigation, and the first results which we obtained seemed so puzzling that we extended our experiments also to *d*-isomenthone.

When *l*-menthone is treated with sodamide and carbon dioxide, under the conditions described on p. 1770, it yields a syrupy monocarboxylic acid, which doubtless has the constitution:

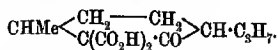


since it gives a purple coloration when ferric chloride is added to its alcoholic solution. The ester of this acid distilled at  $143\text{--}146^\circ/12$  mm., and is evidently structurally identical with the ester which Kötze and Schwarz (*Annalen*, 1907, 357, 210) obtained from ethyl  $\beta$ -methyl- $\epsilon$ -isopropylpimelate by the action of sodium:



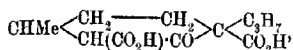
and which distilled at  $145\text{--}149^\circ/14$  mm. and gave a violet coloration with ferric chloride. As well as the above menthonomonocarboxylic acid, a dicarboxylic acid is produced during the action of sodamide and carbon dioxide on *l*-menthone, and this melts

at about 121—128°, and is probably a mixture of the *cis*- and *trans*-modifications of the formula

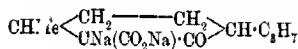


During repeated recrystallisation from ether, much decomposition took place, but we were ultimately successful in obtaining a small quantity of a dibasic acid from the mixture, which melted at 144°, and appears to be one of the above modifications in a pure state.

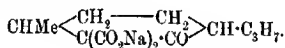
This acid cannot have the constitution:



because its solution in alcohol does not give a coloration with ferric chloride; its formation may be explained in the following manner. The sodium derivative of *isomenthone* is partly converted, by the action of carbon dioxide, into the sodium salt of *isomenthone*-carboxylic acid, which then reacts with some of the unchanged sodium *isomenthone* to yield the disodium derivative:



(or its enolic modification), and this is then converted, by the subsequent action of the carbon dioxide, into the disodium salt of *isomenthonedicarboxylic acid*:



Menthonecarboxylic acids, possessing similar properties to the above, have already been described. In 1891 (*Ber.*, **24**, 3396) Brühl, Biltz, and Cantzler treated ordinary *l*-menthone with sodium wire and carbon dioxide, and obtained a semi-solid mass, which was clearly a mixture of menthone-mono- and -dicarboxylic acids. By treatment with light petroleum, the oily monobasic acid was removed, and was not further investigated, and the insoluble, crystalline residue, after crystallisation from ether, melted at 128.5°, and was shown by analysis to be a menthonedicarboxylic acid. Oddo (*Gazzetta*, 1897, **27**, ii, 97) subsequently investigated the action of sodium and carbon dioxide on *l*-menthone, and obtained a syrupy menthomonocarboxylic acid and a dicarboxylic acid, which melted at 140—141°.

These investigators do not appear to have determined the rotation of their acids, and, when we proceeded to investigate the acids we had prepared, we found that the monobasic as well as the dibasic acids obtained from *l*-menthone were both strongly dextro-rotatory.

This result led us to prepare a quantity of *d*-isomenthone from *l*-menthone by the action of sulphuric acid (Beckmann, *Annalen*, 1888, 250, 334), and on treating this with sodamide and carbon dioxide under exactly the same conditions as before, we found that both the mono- and di-basic acids were again strongly dextro-rotatory.

A large number of experiments were then made with different samples of *l*-menthone and *d*-isomenthone, and the results, which are summarised in the following tables, show that whatever the rotation of the original *l*-menthone or *d*-isomenthone may be, the resulting mono- and di-basic acids are always dextrorotatory, and yield dextro-rotatory isomenthones on distillation.

TABLE I.—*isoMenthonemonocarboxylic Acid*.

Rotation of original menthone, [ $\alpha$ ] <sub>D</sub>	Rotation of the monocarboxylic acid, [ $\alpha$ ] <sub>D</sub>	Rotation of the isomenthone regenerated from the acid, [ $\alpha$ ] <sub>D</sub>
-24.6°	+22.6°	+19.0°
-19.1	+20.8	+17.9
-7.3	+19.4	+17.1
+8.3	+18.4	+16.9
+23.6	+22.5	+18.2
-20.3	+23.7	+15.4
-19.1	+28.3	+15.8

The last two experiments were made under special conditions mentioned on p. 1771.

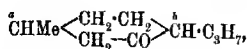
TABLE II.—*isoMenthonedicarboxylic Acid*.

Rotation of original menthone, [ $\alpha$ ] <sub>D</sub>	M. p. of dibasic acid.	Rotation of the dibasic acid, [ $\alpha$ ] <sub>D</sub>	Rotation of the <i>iso</i> - menthone regenerated from the acid, [ $\alpha$ ] <sub>D</sub>
-24.6°	127-128°	+116.5°	—
+23.6	124-125	+107.2	—
-19.1	122-123	+102.4	—
-19.1	115	+100.3	—
-19.1	135	+121.4	+30.2°
-19.1	144	+124.4	+33.3

We next observed that, when *l*-menthone is converted into its sodium derivative by the action of sodamide on its ethereal solution, *d*-isomenthone is obtained on treatment with acids, and also that the latter by similar treatment merely suffers a slight change in rotation. Thus, in two experiments, *l*-menthone with [ $\alpha$ ]<sub>D</sub> -20.3°, after treatment with sodamide, had [ $\alpha$ ]<sub>D</sub> +12.0° and +15.8°, and *d*-isomenthone with [ $\alpha$ ]<sub>D</sub> +14.2°, after treatment with sodamide, had [ $\alpha$ ]<sub>D</sub> +15.8°. It had previously been observed that *l*-menthone is converted at least partly into *d*-isomenthone when

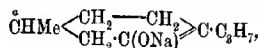
it is treated with concentrated acids or boiled with alcoholic potassium or sodium hydroxide, and these facts and the behaviour summarised in tables I and II may be possibly explained in the following way.

Menthone:



contains two asymmetric carbon atoms, *a* and *b*, and the isomerism of menthone and isomenthone is due to differences in the nature of these.

For the sake of argument the asymmetric carbon atoms in *l*-menthone may be represented by the signs —, and it is clear that when *l*-menthone is converted into its sodium derivative:



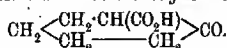
or is treated with any agent which brings about enolic change, the asymmetry of the carbon atom *b* disappears, and the activity of the sodium derivative is due entirely to the carbon atom *a*.

When the sodium derivative is decomposed by acids, the carbon atom *b* again becomes asymmetric, and it is probable that the presence of the active asymmetric carbon atom *a* causes the atom *b* to be produced, to some extent at least, in active form; in other words, an asymmetric synthesis is accomplished. The *d*-isomenthone which is always produced under these conditions is therefore probably a mixture of *a*, *b* = — and — +, the latter predominating.

This explanation accounts, in a simple manner, for the very varying rotations which have been so often observed as the result of preparing different samples of menthone and isomenthone by slightly different methods. Apparently the highest rotations which have been recorded for these substances are *l*-menthone,  $[\alpha]_D - 28.46^\circ$ , and *d*-isomenthone,  $[\alpha]_D + 35.1^\circ$  (Beckmann, *J. pr. Chem.*, 1897, [ii], 55, 24, 28).

It will be seen from table II that the purest specimen of *d*-isomenthonedicarboxylic acid, which we were able to obtain, melted at  $144^\circ$ , and on distillation yielded a *d*-isomenthone with  $[\alpha]_D + 33.3^\circ$ , and which was therefore probably almost pure. On the other hand, it seems doubtful whether *l*-menthone has ever been prepared quite free from *d*-isomenthone.

## EXPERIMENTAL.

*cycloHexanone-2-carboxylic Acid,*

Although this acid is so unstable, we have succeeded in isolating it in some quantity, and have analysed it and determined some of its properties. The details of the preparation are as follows. *cycloHexanone*\* (5 grams) is dissolved in pure dry ether, finely powdered sodamide (2 grams) added, and the mixture warmed until the sodium derivative has completely separated. A current of carbon dioxide, which has been thoroughly washed and very carefully dried, is then passed slowly through the mixture for two to three hours at a temperature of 35°, the whole being well shaken from time to time and great care taken to exclude every trace of moisture. When the reaction is complete, the flask is cooled, and the product decomposed with ice and dilute hydrochloric acid and repeatedly extracted with ether. The ethereal layer is then shaken with a concentrated solution of sodium carbonate, the alkaline solution quickly cooled with powdered ice, acidified with dilute hydrochloric acid, and the *cyclohexanone-2-carboxylic acid*, which separates as an oil, is extracted with ether.

The ethereal solution is dried, the ether partly evaporated on steam-bath under diminished pressure, and the remainder allowed to evaporate in the air, when crystals of the acid are gradually deposited.

These are left in contact with porous porcelain until quite dry, and then recrystallised from ether:

0.1438 gave 0.3105 CO<sub>2</sub> and 0.0919 H<sub>2</sub>O. C=58.9; H=7.1.

C<sub>7</sub>H<sub>10</sub>O<sub>3</sub> requires C=59.1; H=7.0 per cent.

On titration with *N*/10-sodium hydroxide, 0.1314 neutralised 0.0504 NaOH, whereas this amount of a monobasic acid, C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>, should neutralise 0.0512 NaOH.

*cycloHexanone-2-carboxylic acid* softens at 79°, and decomposes at 81–82° into *cyclohexanone* and carbon dioxide. It is readily soluble in water, and the aqueous solution gives a deep violet coloration on the addition of ferric chloride. It dissolves readily in ether, alcohol, benzene, or light petroleum, and separates from ether in glistening needles.

*Reduction to cycloHexanol-2-carboxylic acid (hexahydrocyclohexanecarboxylic acid)*

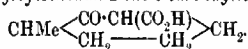
\* The *cyclohexanone* employed in these experiments was obtained from Paulenc Frères, and carefully purified by conversion into the sodium hydrogen sulphite derivative; it distilled at 155–156°/755 mm. and crystallised readily.

acid).—Preliminary experiments showed that in many cases the carboxylic acids of *cyclohexanone* and its derivatives are either not reduced at all by sodium amalgam under ordinary conditions, or, if reduced, that the process is extremely slow and often incomplete. The following modification yields, however, in most cases, excellent results.

*cycloHexanone-2-carboxylic acid* (5 grams) is dissolved in a dilute solution of sodium carbonate, freshly prepared 3 per cent. sodium amalgam (300 grams) is slowly added, and the solution kept nearly neutral by passing a slow current of sulphur dioxide.

The product is acidified and extracted once or twice with ether in order to remove traces of unreduced keto-acid, the liquid is then saturated with ammonium sulphate, and extracted several times on the machine. The extract is dried and evaporated, and the solid mass of *cyclohexanol-2-carboxylic acid* left in contact with porous porcelain, and then crystallised from ether, from which the acid separates in glistening prisms melting at  $111^{\circ}$ . (Found, C=58.0; H=8.2. Calc., C=58.3; H=8.3 per cent.)

1-Methylcyclohexan-2-one-3-carboxylic Acid,



The 1-methylcyclohexan-2-one used in these experiments was prepared by ourselves from o-cresol by the Sahatier-Senderens process, and then very carefully separated from 1-methylcyclohexan-2-ol and other impurities by conversion into the sodium hydrogen-sulphito derivative. It distilled at  $164\text{--}165^{\circ}$  (compare Wallach, *Annalen*, 1906, **346**, 251). The conversion into the sodium derivative by means of sodamide and the subsequent treatment with carbon dioxide was carried out at the ordinary temperature in the manner described on p. 1764, carefully purified light petroleum being used as the solvent in the place of ether. The product was mixed with powdered ice and dilute hydrochloric acid, the oily acid extracted with ether, the ethereal solution rapidly dried, and the ether distilled off under diminished pressure. The residual pale yellow syrupy acid, which showed no tendency to crystallise, was at once analysed, and yielded numbers agreeing so well with those required by theory that there can be no doubt that the syrup consisted of practically pure 1-methylcyclohexan-2-one-3-carboxylic acid.

It is unfortunate that the yield of acid obtained by the above method of preparation is very small, and we have so far been unsuccessful in our attempts to discover better conditions. The



following analyses were carried out with acid obtained from two preparations:

0.2451 gave 0.5535  $\text{CO}_2$  and 0.1755  $\text{H}_2\text{O}$ .  $\text{C} \approx 61.6$ ;  $\text{H} \approx 8.0$ .

0.1471 " 0.3325  $\text{CO}_2$  " 0.1042  $\text{H}_2\text{O}$ .  $\text{C} \approx 61.7$ ;  $\text{H} \approx 7.9$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.5$ ;  $\text{H} = 7.7$  per cent.

Ethyl 1-methylcyclohexan-2-one-3-carboxylate was obtained in a very small yield by leaving the syrupy keto-acid in contact with 5 per cent. alcoholic sulphuric acid for twenty-four hours. It was isolated in the usual manner (p. 1767), and distilled at about  $125\text{--}130^\circ/20$  mm. (Found,  $\text{C} = 64.9$ ;  $\text{H} = 8.8$ . Calc.,  $\text{C} = 65.2$ ;  $\text{H} = 8.7$  per cent.)

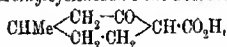
Kötz and Michels (*Annalen*, 1906, **348**, 94), who obtained this ester by a different process (p. 1759), state that it distills at  $115^\circ/12$  mm. We have also made a series of experiments on the reduction of 1-methylcyclohexan-2-one-3-carboxylic acid by sodium amalgam and sulphurous acid, using the conditions so successfully employed in other cases (p. 1765), but the product was always an almost colourless syrup, which could not be made to crystallise. That this syrup, which gave no coloration with ferric chloride, consisted of 1-methylcyclohexan-2-ol-3-carboxylic acid, is indicated by the following analysis:

0.1450 gave 0.3222  $\text{CO}_2$  and 0.1144  $\text{H}_2\text{O}$ .  $\text{C} = 60.5$ ;  $\text{H} = 8.3$ .

$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C} = 60.8$ ;  $\text{H} = 8.9$  per cent.,

and the fact that the acid could not be obtained in a crystalline condition may be due, in part, to its being a mixture of stereoisomeric modifications.

dl- and d-l-Methylcyclohexan-3-one-4-carboxylic Acid,



and the corresponding 1-Methylcyclohexan-3-ol-4-carboxylic Acid.

dl-1-Methylcyclohexan-3-one-4-carboxylic acid was prepared from pure inactive 1-methylcyclohexan-3-one obtained from Kahlbaum.

The ketone (14 grams), dissolved in light petroleum, was mixed with powdered sodamide (5 grams), when rapid evolution of ammonia took place and the white sodium derivative separated. As soon as decomposition was complete, a rapid stream of dry carbon dioxide was passed, the whole being vigorously stirred during the operation.

The temperature rose rapidly to about  $45^\circ$  and then gradually subsided, and, as soon as the mass was quite cold, the stream of gas was interrupted. The product was treated with ice and hydrochloric acid in the usual manner, ether was then added, the ether-

petroleum layer separated, extracted with sodium carbonate, and the alkaline solution acidified, when an oil separated, which rapidly crystallised.

The crystals were collected and purified by reprecipitation from the sodium salt, and then by crystallisation from ether:

0.1700 gave 0.3817  $\text{CO}_2$  and 0.1194  $\text{H}_2\text{O}$ .  $\text{C}=61.2$ ;  $\text{H}=7.3$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C}=61.5$ ;  $\text{H}=7.7$  per cent.

*dl*-1-Methylcyclohexan-3-one-4-carboxylic acid separates from ether in prisms, and melts and decomposes at about  $100-103^\circ$ .

It is readily soluble in ether or alcohol, and moderately readily so in benzene or light petroleum, but it is rather sparingly soluble in cold water; the alcoholic solution gives with ferric chloride an intense violet coloration.

*Ethyl dl*-1-methylcyclohexan-3-one-4-carboxylate was prepared by leaving the acid in contact with a large excess of 5 per cent. alcoholic sulphuric acid for twenty-four hours, and then precipitating with water.

The oil was extracted with ether, the ethereal solution washed with sodium carbonate, dried, and fractionated, when practically the whole quantity distilled at  $132-135^\circ/24$  mm., and gave an intense violet coloration when ferric chloride was added to the alcoholic solution:

0.1873 gave 0.4461  $\text{CO}_2$  and 0.1483  $\text{H}_2\text{O}$ .  $\text{C}=64.9$ ;  $\text{H}=8.8$ .

$\text{C}_{16}\text{H}_{20}\text{O}_4$  requires  $\text{C}=65.2$ ;  $\text{H}=8.7$  per cent.

*dl*-1-Methylcyclohexan-3-ol-4-carboxylic acid.—In preparing this acid, the pure *dl*-keto-acid (5 grams), dissolved in a slight excess of dilute sodium carbonate, was mixed with freshly prepared 3 per cent. sodium amalgam (500 grams) all at once, in an apparatus fitted with a mechanical stirrer, carbon dioxide being passed during the whole operation. The product was extracted in the usual manner, and again treated with sodium amalgam exactly as before, when an acid was obtained, which was at first oily, but gradually crystallised.

It was purified by crystallisation from ether, from which it separated in elongated prisms:

0.1412 gave 0.3132  $\text{CO}_2$  and 0.1120  $\text{H}_2\text{O}$ .  $\text{C}=60.5$ ;  $\text{H}=8.8$ .

$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C}=60.8$ ;  $\text{H}=8.8$  per cent.

*dl*-1-Methylcyclohexan-3-ol-4-carboxylic acid melts at  $130-131^\circ$ , and is readily soluble in alcohol and moderately so in water, benzene, or chloroform. The alcoholic solution gives no coloration on the addition of ferric chloride.

*d*-1-Methylcyclohexan-3-one-4-carboxylic Acid.—The *d*-1-methylcyclohexan-3-one, employed in the preparation of this acid, was

obtained from Schimmel & Co., and had been prepared from pulegone by hydrolysis (Wallach, *Annalen*, 1896, **289**, 339); it had  $[\alpha]_D + 8.8^\circ$ .

This ketone was converted into *d*-1-methylcyclohexan-3-one-4-carboxylic acid in the manner already described in the case of the *dl*-acid, and the *d*-acid, thus obtained, separated from ether in small, and from light petroleum in large, prisms when the solutions in these solvents were allowed to concentrate slowly at the ordinary temperature:

0.1310 gave 0.2967  $\text{CO}_2$  and 0.0935  $\text{H}_2\text{O}$ .  $\text{C} = 61.3$ ;  $\text{H} = 7.8$ .

$\text{C}_8\text{H}_{12}\text{O}_3$  requires  $\text{C} = 61.5$ ;  $\text{H} = 7.7$  per cent.

The basicity was determined by titration with *N*/10 sodium hydroxide, when 0.3055 neutralised 0.0775  $\text{NaOH}$ , whereas this amount of a monobasic acid,  $\text{C}_8\text{H}_{12}\text{O}_3$ , should neutralise 0.0784  $\text{NaOH}$ .

*d*-1-Methylcyclohexan-3-one-4-carboxylic acid melts at about  $102-103^\circ$ , and gives a purple coloration when ferric chloride is added to its alcoholic solution.

0.4795, made up to 20 c.c. with alcohol, gave  $\alpha_D + 4.66^\circ$  in a 2-dcm. tube at  $17^\circ$ , whence  $[\alpha]_D + 97.2^\circ$ .

Several grams of the acid were heated in a small retort until decomposed, when it was found that the 1-methylcyclohexan-3-one which distilled over boiled at  $169^\circ$ , and had  $[\alpha]_D + 8.8^\circ$ , showing that no change in rotation had occurred during the conversion into the acid and subsequent elimination of carbon dioxide. *Ethyl d*-1-methylcyclohexan-3-one-4-carboxylate, prepared in the same manner as the *dl*-ester, distilled at  $134-137^\circ/26$  mm.:

0.2115 gave 0.5033  $\text{CO}_2$  and 0.1694  $\text{H}_2\text{O}$ .  $\text{C} = 64.9$ ;  $\text{H} = 8.9$ .

$\text{C}_{10}\text{H}_{16}\text{O}_3$  requires  $\text{C} = 65.2$ ;  $\text{H} = 8.7$  per cent.

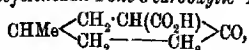
0.5423, made up to 25 c.c. with alcohol, gave  $\alpha_D + 3.49^\circ$  in a 2-dcm. tube at  $17.5^\circ$ , whence  $[\alpha]_D + 84.16^\circ$ .

*d*-1-Methylcyclohexan-3-ol-4-carboxylic acid, prepared by the reduction of the *d*-keto-acid with sodium amalgam exactly as described in the case of the *dl*-acid, melts at  $129-130^\circ$ :

0.1480 gave 0.3290  $\text{CO}_2$  and 0.1187  $\text{H}_2\text{O}$ .  $\text{C} = 60.6$ ;  $\text{H} = 8.8$ .

$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C} = 60.8$ ;  $\text{H} = 8.8$  per cent.

0.1023, dissolved in alcohol and made up to 25 c.c., gave  $\alpha_D - 2.6^\circ$  in a 2-dcm. tube at  $17^\circ$ , whence  $[\alpha]_D - 31.8^\circ$ .

*1-Methylcyclohexan-4-one-3-carboxylic Acid,*

and its Reduction to *1-Methylcyclohexan-4-ol-3-carboxylic Acid.*

*1-Methylcyclohexan-4-one*, obtained from Poulenc Frères, was found to contain *methylcyclohexanol*, and it was therefore purified by conversion into the sodium hydrogen sulphite derivative, and the regenerated ketone, which distilled at 169–170°, was employed in the following experiments. The conversion of the ketone into the carboxylic acid, by the action of sodamide and carbon dioxide, was carried out practically under the conditions which are described in detail in the case of the preparation of *1-methylcyclohexan-3-one-4-carboxylic acid* (p. 1766). When the solution of the sodium salt was acidified, the acid was at once precipitated as a solid, and was readily purified by recrystallisation from ether, the pure acid being thus obtained in a yield of about 40 per cent. of that theoretically possible:

0.1110 gave 0.2500 CO<sub>2</sub> and 0.0780 H<sub>2</sub>O. C=61.4; H=7.9.

0.1231 „ 0.2769 CO<sub>2</sub> „ 0.0860 H<sub>2</sub>O. C=61.3; H=7.7.

C<sub>8</sub>H<sub>10</sub>O<sub>3</sub> requires C=61.5; H=7.7 per cent.

*1-Methylcyclohexan-4-one-3-carboxylic acid* separates from ether in prisms, and melts at 101°; it is readily soluble in alcohol, ether, or chloroform, but rather sparingly so in cold water; the addition of ferric chloride to the alcoholic solution produces a purple coloration which becomes rather bluer on the addition of a little water.

Ethyl *1-methylcyclohexan-4-one-3-carboxylate* was prepared by leaving the finely divided acid (20 grams) in contact with excess of 5 per cent. alcoholic sulphuric acid (150 c.c.) for two days, and then precipitating with water. The ester was extracted with ether, the ethereal solution washed with sodium carbonate, dried, and distilled, when, after much *methylcyclohexanone* had passed over, the ester distilled at 128–130°/20 mm. (Found, C=65.5; H=8.9. Calc., C=65.2; H=8.7 per cent.)

Kötz and Michels (*Annalen*, 1906, 348, 95) who obtained this ester by a different method (compare p. 1759), state that it distils at 110°/10 mm.

*1-Methylcyclohexan-4-ol-3-carboxylic acid* is obtained when the solution of the keto-acid in sodium carbonate is reduced by sodium amalgam at about 40–50° in an apparatus fitted with a mechanical stirrer, carbon dioxide being passed during the operation.

The product was acidified with dilute hydrochloric acid and repeatedly extracted with ether, the ethereal solution was dried

and evaporated, when a syrupy acid remained, which gradually became semi-solid. After contact with porous porcelain for several days, the almost colourless, crystalline mass was recrystallised from ether:

0.1200 gave 0.2670  $\text{CO}_2$  and 0.0952  $\text{H}_2\text{O}$ .  $\text{C}=60.7$ ;  $\text{H}=8.9$ .

$\text{C}_8\text{H}_{14}\text{O}_3$  requires  $\text{C}=60.8$ ;  $\text{H}=8.8$  per cent.

1-Methylcyclohexan-4-ol-3-carboxylic acid separates from ether as a hard, crystalline crust and melts at  $114^\circ$ ; it is readily soluble in water or alcohol, but sparingly so in cold ether.

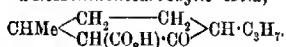
Ethyl 1-Methylcyclohexan-4-ol-3-carboxylate.—In preparing this ester, the porous plates used in the purification of the crude hydroxy-acid were extracted in a Soxhlet apparatus, and the syrupy extract was dissolved in a large excess of 10 per cent. alcoholic sulphuric acid. After several days, the product was mixed with water, the ester extracted with ether, the ethereal solution washed with sodium carbonate, dried, and evaporated, and the ester purified by fractionation, when it distilled constantly at  $132\text{--}134^\circ/17$  mm.:

0.1083 gave 0.2559  $\text{CO}_2$  and 0.0977  $\text{H}_2\text{O}$ .  $\text{C}=64.4$ ;  $\text{H}=10.1$ .

$\text{C}_{10}\text{H}_{18}\text{O}_3$  requires  $\text{C}=64.5$ ;  $\text{H}=9.7$  per cent.

When this ester was hydrolysed by methyl-alcoholic potassium hydroxide, it yielded at once the hydroxy-acid in a crystalline form, and probably the best way of purifying this acid in future will be to convert the crude product of the reduction of the keto-acid at once into the ester, and, after distilling this, to regenerate the acid by hydrolysis.

*d*-isoMenthonecarboxylic Acid,



In our first experiments on the behaviour of menthone on treatment with sodamide and carbon dioxide, the *l*-menthone employed had  $[\alpha]_D -24.6^\circ$ . This (20 grams) was dissolved in light petroleum and mixed with powdered sodamide (5 grams), when evolution of ammonia took place, and the soluble sodium derivative was readily produced.

A current of dry carbon dioxide was then passed through the solution for half an hour, without external cooling, and the product decomposed by ice and water. The aqueous layer was separated, acidified with hydrochloric acid, and, after saturating with ammonium sulphate, extracted with ether. The ethereal solution was shaken with cold sodium carbonate, the alkaline solution acidified, and well shaken with light petroleum (b. p.  $40\text{--}60^\circ$ ),

which extracts the monobasic acid. The extract was again treated with sodium carbonate, and the extraction with light petroleum repeated; finally the petroleum was distilled off under diminished pressure, the last traces being removed in a vacuum. The almost colourless syrup was at once analysed, with the following result:

0.1968 gave 0.4783  $\text{CO}_2$  and 0.1647  $\text{H}_2\text{O}$ .  $\text{C}=66.3$ ;  $\text{H}=9.3$ .

$\text{C}_{11}\text{H}_{18}\text{O}_3$  requires  $\text{C}=66.7$ ;  $\text{H}=9.1$  per cent.

0.6287, made up to 20 c.c. with alcohol, gave  $\alpha_D +1.42^\circ$  in a 2-dcm. tube at  $16^\circ$ , whence  $[\alpha]_D +22.6^\circ$ .

When the acid was distilled, it was readily decomposed with elimination of carbon dioxide, and the determination of the rotation of the isomenthone obtained gave the following result:

1.0268, made up to 20 c.c. with alcohol, gave  $\alpha_D +1.95^\circ$  in a 2-dcm. tube at  $16^\circ$ , whence  $[\alpha]_D +19.0^\circ$ .

A large number of similar experiments were made on the action of sodamide and carbon dioxide on various specimens both of *i*-menthone and of *d*-isomenthone, but, as the results of these are summarised in table I (p. 1762), it is unnecessary to give full details. One point of some interest may, however, be mentioned. In the first five experiments given in the table, the temperature was allowed to rise during the passage of the carbon dioxide through the solution of the sodium derivative in light petroleum, whereas, in the last two, which gave monocarboxylic acids of the highest rotations, the rise of temperature was prevented by surrounding the vessel containing the sodium derivative with ice. *d*-isoMenthonecarboxylic acid is an unstable substance, which slowly decomposes into *d*-isomenthone and carbon dioxide even at the ordinary temperature; its solution in alcohol gives with ferric chloride an intense purple coloration.

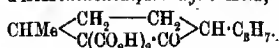
*d*-isoMenthonecarboxylic acid is produced when *d*-isomenthonecarboxylic acid (5 grams), dissolved in cold dilute sodium carbonate, is treated with 3 per cent. sodium amalgam (500 grams). The product was first extracted with ether in order to remove traces of neutral oil, then acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. After drying and evaporating, a syrupy acid was obtained, which did not show any signs of crystallising, but that reduction had taken place was proved by the fact that the solution of the acid in alcohol did not give any coloration on the addition of ferric chloride:

0.2276 gave 0.5493  $\text{CO}_2$  and 0.2069  $\text{H}_2\text{O}$ .  $\text{C}=65.8$ ;  $\text{H}=10.1$ .

$\text{C}_{11}\text{H}_{20}\text{O}_3$  requires  $\text{C}=66.0$ ;  $\text{H}=10.0$  per cent.

0.4990, made up to 25 c.c. with alcohol, gave  $\alpha_D +0.48^\circ$  in a 2-dcm. tube at  $16^\circ$ , whence  $[\alpha]_D +12.0^\circ$ .

*d*-isoMenthonedicarboxylic Acid,



This acid is always produced along with the monocarboxylic acid when the conditions described in the last section are observed, and is extracted with ether after the removal of the monobasic acid.

The ethereal solution was shaken with a little sodium carbonate, and the acid precipitated, when it separated at first as an oil, which, however, rapidly crystallised. After the removal of traces of oily impurity by contact with porous porcelain and once crystallising from ether, the colourless mass melted at 121–128°.

By repeatedly crystallising from ether, a small quantity of the dibasic acid was obtained, which melted at 144°, but the loss during recrystallisation, due to elimination of carbon dioxide, was serious:

0.152 gave 0.3310 CO<sub>2</sub> and 0.1033 H<sub>2</sub>O. C=59.4; H=7.5.

C<sub>12</sub>H<sub>18</sub>O<sub>6</sub> requires C=59.5; H=7.4 per cent.

0.3456, made up to 20 c.c. with alcohol, gave α<sub>D</sub> +4.3° in a 2-dcm. tube, whence [α]<sub>D</sub> +124.4°.

When this specimen was distilled, it yielded a *d*-isomenthone, of which the rotation was determined.

0.3662, made up to 20 c.c. with alcohol, gave α<sub>D</sub> +1.22° in a 2-dcm. tube at 17°, whence [α]<sub>D</sub> +33.3°.

*d*-isoMenthonedicarboxylic acid is readily soluble in alcohol or ethyl acetate, moderately so in acetone, chloroform, or water, and the alcoholic solution is not immediately coloured by the addition of ferric chloride. If the solution is kept, a faint violet coloration appears after some minutes, and this gradually deepens, a change which is doubtless due to the slow elimination of carbon dioxide and consequent formation of the monocarboxylic acid. Several specimens of this dicarboxylic acid were prepared from menthones of widely different rotations, and the results of these experiments are summarised in table II (p. 1762).

The authors are indebted to Dr. Lapworth for valuable suggestions made during the progress of this research, and they also wish to state that much of the expense was met by grants from the Research Fund of the Chemical Society.

THE UNIVERSITY,  
MANCHESTER.

CLXXXVII.—*cycloHexane, its Separation from, and its Estimation in, Mixtures containing Benzene.*

By THOMAS STEWART PATTERSON and ALEXANDER FLECK.

WHEN *cyclohexane* is prepared from benzene there is considerable difficulty both in separating the two substances by physical means, since their properties are so much alike, and in estimating the quantity of unchanged benzene in the product of reduction. It is usually recommended either to nitrate the benzene or to sulphonate it, but both processes are rather troublesome and are extravagant as regards time.

In connexion with the preparation, by the Sabatier-Senderens method, of a quantity of *cyclohexane*, the purity of which we had no ready means of ascertaining, it occurred to us that a simple method of analysis might possibly be based on an anticipated difference in the solvent influence on the rotation of ethyl tartrate, of benzene on the one hand, and *cyclohexane* on the other, since it has been shown repeatedly that the optical activity of ethyl tartrate varies, often to a very great extent, in accordance with comparatively slightly differences in composition or constitution of the solvent.

Our proposal, therefore, was to make a solution in benzene and a solution in *cyclohexane* of ethyl tartrate, and to determine the rotation of each. If there were a considerable difference, then the composition of a mixture of *cyclohexane* and benzene could be ascertained by making an equally concentrated solution of ethyl tartrate in the mixture, measuring its rotation, and, by interpolation, estimating the relative proportions of its constituents.

We came across an unexpected but not unwelcome difficulty at the outset, when we found that *cyclohexane* and ethyl tartrate are practically immiscible liquids, and therefore a very simple method of purification presented itself at once. When the quantity of benzene is small, the mixture need only be shaken up with about its own volume of ethyl tartrate, once or oftener, as seems necessary. When, however, benzene is present to the extent of about 50 per cent., some care must be exercised. Too much ethyl tartrate must not be used, or a homogeneous mixture will result. In connexion with the experiments quoted below, we found that four volumes of ethyl tartrate with one volume of benzene and one volume of *cyclohexane* give a homogeneous mixture, but if only one volume of ethyl tartrate be used, the mixture separates into two layers. To test this method of separation, we made up a mixture of benzene and *cyclohexane* in equal proportions. A quantity of this



solution was shaken with half its volume of ethyl tartrate, and the whole cooled in a freezing mixture of ice and salt. The upper layer was then separated and shaken with about its own volume of ethyl tartrate, separated again, and distilled. Approximately 50 per cent. of the original *cyclohexane* was recovered in a pure condition. If a mixture contains more than about 50 per cent. of benzene, its separation by shaking with ethyl tartrate would be distinctly more difficult, but could perhaps be accomplished by the addition of a little water to the mixture; we have not, however, attempted such a separation.

On account of this difficulty in regard to solubility, it was necessary to alter our proposed method of estimation in order to obtain an active liquid with which *cyclohexane* would mix. We finally adopted a mixture of four volumes of ethyl tartrate and one volume of benzene, as we found that five volumes of this solution mix completely with one volume of *cyclohexane*.

We therefore made up several solutions all containing 4 c.c. of ethyl tartrate and 1 c.c. of benzene (5 c.c. of a stock solution), and then one other c.c. of variable composition, either pure benzene, pure *cyclohexane*, or a mixture of the two in known proportions.

The rotation of each solution was then determined in a 50 mm. tube, the temperature being kept constant at 25°.

The results were as follows:

Volume percentage of <i>cyclohexane</i> in the variable c.c. ....	0	20	40	60	80	100
$\alpha_D^{25}$ .....	+2.81°	2.53°	2.40°	2.21°	2.09°	1.76°
Deviation from mean .....	$\pm 0.00^\circ$	-0.02°	+0.015°	+0.03°	+0.03°	$\pm 0.06^\circ$

Thus a solution containing 4 vols. of ethyl tartrate and 2 vols. of benzene gives a rotation of +2.81°; one of 4 vols. of ethyl tartrate, 1 vol. of benzene, and 1 vol. of *cyclohexane* gives a rotation of +1.76°. The substitution of 1 vol. of *cyclohexane* for 1 vol. of benzene brings about therefore a diminution of 1.05° in rotation. Benzene has only a slight effect on the rotation of ethyl tartrate, so that *cyclohexane* must have a considerable depressing influence, since a small proportion of it is capable of reducing the rotation of the above solution by about 33 per cent.

The total difference of 1.05° is, however, not very much to work upon, but since the polarimeter can be read to 0.01°, it should be possible, using great care, to reduce the error of an estimation by this method to about 1 per cent. By using larger quantities of substance and a longer polarimeter tube, an accuracy of 1 per cent. should not be difficult to attain to. If our data be plotted on a diagram, it will be seen that the intermediate values lie about the

straight line \* joining the two extremes. Assuming that the end values are correct, the maximum deviation from the straight line is  $+0.03^\circ$ , whence these experiments may be relied on to about 3 per cent.

In order to test our method of analysis, one observer prepared a mixture of benzene and *cyclohexane*, which was then examined by the other observer. One c.c. of the mixture was added to 5 c.c. of the stock solution. The rotation of this solution was  $+2.39^\circ$ , which should correspond with 39.5 per cent. of *cyclohexane*. The solution actually contained 35.7 per cent., so that the error was 3.8 per cent. The experiment had involved the use of a 1 c.c. pipette not used in the other set of observations, and this may account for the slightly increased error.

The product of our Sabatier-Senderens reaction was now shaken with about half its volume of ethyl tartrate. Some 90 to 92 per cent. of the preparation remained undissolved. This was separated and redistilled. Its boiling point was  $80^\circ$ . One c.c. of this was mixed with 5 c.c. of the stock solution of ethyl tartrate and benzene, and the resulting liquid examined as before in the polarimeter. It always happened—~~we~~ tried the experiment several times—that the value of the rotation started about  $+1.90^\circ$ , and fell gradually during a period of approximately eighteen hours to the value  $1.75$ – $1.76^\circ$ , the latter being the rotation previously found for the solution containing 1 c.c. of pure *cyclohexane*. These solutions were homogeneous, and, when placed in a freezing mixture, did not separate into two layers. The *cyclohexane* was again shaken with ethyl tartrate, separated, and distilled, but the same behaviour as before was observed when its solution with benzene—ethyl tartrate was examined in the polarimeter. We are unable to suggest an explanation of this curious phenomenon. Solutions made up by mixing *cyclohexane* (Kahlbaum) with ethyl tartrate and benzene did not show it.

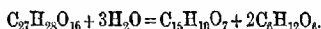
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\* In general, this would doubtless not be a straight line. See Trans., 1909, 95, 1131.

CLXXXVIII.—*The Identity of Osyritrin, Myrticolarin, Violaquercitrin, and Rutin.*

By ARTHUR GEORGE PERKIN.

In a previous communication (Trans., 1902, 81, 477) it was shown that osyritrin (*Osyris compressa*), myrticolarin (*Eucalyptus macroryncha*, Smith, Trans., 1893, 73, 697), and violaquercitrin (*Viola tricolor*, Mandelin, *Jahresb.*, 1883, 1369) were identical, and the formula  $C_{27}H_{28}O_{16}$  was assigned to these substances. From the products of their hydrolysis, quercetin and dextrose (as osazone) were isolated, and this decomposition was represented by the equation:



The close resemblance of osyritrin to rutin was noted at the time, for it was pointed out that the dyeing properties of these glucosides are identical, and in an earlier paper (Trans., 1899, 75, 440) that both compounds yield a monopotassium salt of similar character. On the other hand, as, according to Beilstein (*Handbuch*, 1897, III, 607), the formula of rutin was  $C_{27}H_{32}O_{16} \cdot 2H_2O$ , its melting point above  $190^\circ$ , and the products of its hydrolysis quercetin and two molecules of rhamnose (Schunck, Trans., 1883, 53, 264), it appeared unnecessary to carry out a further comparison of these two compounds. A more recent investigation by Schmidt (*Arch. Pharm.*, 1908, 246, 214) and also by Wunderlich (*ibid.*, 246, 224) has, however, shown that violaquercitrin is identical with rutin, and that, moreover, both compounds, when hydrolysed, give not only dextrose but rhamnose:



From the fact of the identity of osyritrin, myrticolarin, and violaquercitrin, it was obvious that these three glucosides consisted of rutin, and a further examination of this point did not suggest itself. The appearance of a paper by Auld (Proc., 1910, 26, 146) on the presence of osyritrin in the *Osyris abyssinica*, and a private communication from Dr. G. Clarke as to the existence of a substance apparently identical with osyritrin in the leaves of the *Tephrosia purpurea*, but which, however, on hydrolysis, gives quercetin, dextrose, and rhamnose, has shown that a further note on this subject is necessary.

Experiments have been therefore carried out to prove that when hydrolysed, myrticolarin and osyritrin give not only dextrose but rhamnose. Some quantity of the former was prepared in a pure

condition from the residue of a commercial sample\* received some time ago from Mr. H. G. Smith for a determination of its practical value, and this was digested with boiling dilute-sulphuric acid in the usual manner. The filtrate from the quercetin was neutralised with barium carbonate, the clear liquid partly evaporated, and divided into two portions, the first of which was devoted to the preparation of osazone, and the second to the isolation of rhamnose.

The moist osazone washed with ether or acetone gave, as previously found, almost pure glucosazone, and it was owing to this procedure that the more soluble compound, considered to be an impurity, was previously not recognised. The crude substance dissolved in alcohol was now poured into about ten times its bulk of ether, and the solution thoroughly washed with water. By gentle evaporation, the main bulk of the glucosazone separated, and by further fractional distillation a more soluble compound was isolated, which, after purification, melted at  $180-182^{\circ}$ , and had the properties of rhamnosazone.

The second portion of the mixed sugar solution was treated with yeast, and when fermentation had ceased, the filtered liquid was evaporated to dryness. A concentrated alcoholic extract of the residue was inoculated with a crystal of rhamnose, and after two days deposited a considerable quantity of a colourless, crystalline substance. This was collected, washed with a mixture of ether and alcohol, and then melted at  $92-93^{\circ}$ , and this melting point was unaltered by its admixture with rhamnose itself.

For the examination of osyritrin, but 0.5 gram was available, and the preparation of crystalline rhamnose from this glucoside could not be attempted. The osazone of the mixed sugars isolated in the usual manner, however, yielded by fractional crystallisation from ether according to the method above described a substance melting at  $180-183^{\circ}$ , which was evidently rhamnosazone.

Finally, it was found that the melting points of osyritrin and myrticolorin were not affected by admixture with rutin. The formula  $C_{27}H_{28}O_{16} \cdot 3H_2O$ , previously assigned to these preparations, should therefore be  $C_{27}H_{30}O_{16} \cdot 3H_2O$ , and with this the analytical figures given are in equally good agreement.

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\* The simplicity with which myrticolorin can be isolated from the *E. macrorhyncha* in large quantity (Smith, *loc. cit.*) suggested a commercial possibility for this material. Although commercial trials have indicated that, especially on cotton, it is inferior to flavine (quercitrin), it is an excellent source of quercetin, and may eventually possess value in this respect.

CLXXXIX.—*Solubilities of Organic Substances in Organic Solvents: A Contribution to the Theory of Solubility.*

By DAN TYRER.

IN a previous paper (this vol., p. 621) on the solubility of salts above the critical point, it was shown that the solubility above this point varied with the density of the solvent, and could be represented as a function of the concentration of the solvent, that is, the amount of solvent contained in unit volume of the saturated solution. As the concentration of the solvent diminished, the solubility of the solute decreased. This suggests the idea that the concentration of the solvent is an important factor influencing the solubility of a solute. With rise of temperature, the concentration of a solvent in a saturated solution decreases, whereas the solubility of the solute usually increases. We must conclude from this that the solubility is influenced by a second factor, namely, temperature. Considering, then, the solubility of a particular solute in a particular solvent, we can say that the solubility under all possible conditions is governed by the following factors:

- (1) Temperature;
- (2) The concentration of the solvent;

or, expressed mathematically,

$$S = Kf(C) \cdot \phi(T),$$

where  $S$  is the solubility,  $C$  the concentration of the solvent,  $T$  the temperature, and  $K$  a constant.

The object of this work was to determine the form of the function  $f(C)$ .

It must be remarked that the above generalisations are independent of the mode or nature of the process of dissolution, and should be valid for all solutions. At the same time, however, if any comparison is to be made of the form of the function  $f(C)$  for one solution with the form for another, the two solutions must be the same as regards their constitution. That is to say, there must be no polymerisation or association of the molecules of any kind in either of the solutions. For this reason, the solubilities of organic substances in organic solvents, in which the existence of molecular associations is improbable, have been investigated.

In the majority of aqueous solutions, and probably in all solutions where the solvent is an associated liquid, as, for example, a solvent containing a hydroxyl group, molecular association of the solvent and solute undoubtedly occurs, and the process of dissolution in

these cases is probably due to some extent to the formation of these complex molecules. With non-associated solvents, there is evidence for the belief that the solute (if it is also non-associated) does not associate with the solvent, but the molecules of both move freely among each other like the molecules in a mixed gas.

Forch (*Ann. Physik*, 1905, [iv], 17, 1012) found that naphthalene dissolved in non-associated solvents had a constant molecular volume at constant temperature independent of the solvent or the concentration. Such a regularity as this would not exist were there any appreciable molecular association in these solutions. Furthermore, in contrast with associated liquids, when two non-associated liquids are mixed, very small volume and temperature changes occur (Linebarger, *Amer. Chem. J.*, 1896, 18, 440; Brown, *Trans.*, 1881, 39, 202; Thorpe and Rodger, *Trans.*, 1897, 71, 367; Walker and Henderson, *Trans. Roy. Soc. Canada*, 1902, [ii], 8, Sect. iii, 105). This can only be regarded as indicating that no molecular association occurs when non-associated substances are mixed.

From theoretical considerations regarding the form of the composition—partial pressure curve of a constituent of a binary mixture of liquids—Dolezalek (*Zeitsch. physikal. Chem.*, 1908, 64, 727) concluded, from existing data, that in binary mixtures of such liquids as benzene, toluene, chloroform, and in general liquids which are not associated in a pure state, there is no association or polymerisation of any kind.

In order therefore that any regularities which might exist would not be concealed by complications arising from molecular associations, it was necessary to study solubilities of non-associating organic solutes in non-associating organic solvents. General experience leads us to believe that such substances are those not containing hydroxyl, amino-, or cyano-groups. Except in the case of solutions above the critical point, where the concentration of the solvent can be varied at will, only one method of attacking the problem seems available. A solute satisfying the above conditions is found which is soluble in a solvent A, and very slightly soluble (compared with solubility in A) in another solvent B, which is completely miscible with A. B is then used to dilute A, and solubilities in mixtures of A and B in varying proportions from pure A to pure B determined at constant temperature. A determination of the density of the saturated solution is also necessary in order to calculate the concentration of each of the solvents.

An approximation is then made by supposing the amount of the solute dissolved by the B portion of the mixture to be proportional to the concentration of the solvent B. This amount subtracted from the total amount dissolved by the mixture gives the amount

dissolved by A alone. Any error thus introduced will be negligibly small if there is a considerable difference in the solubilities in the respective pure solvents except at low concentrations of A. It must be pointed out that the assumption is here made that the solvent B has no other effect than that of merely diluting A. The necessary conditions greatly restrict the number of cases open to investigation, and only one class of liquids has been found which can be used as diluents. These are the aliphatic hydrocarbons, in which, as a general rule, organic substances of the above specified nature are much less soluble than in other organic solvents.

Incidentally, some careful measurements of the solubility of some organic substances in organic solvents at varying temperatures have been made.

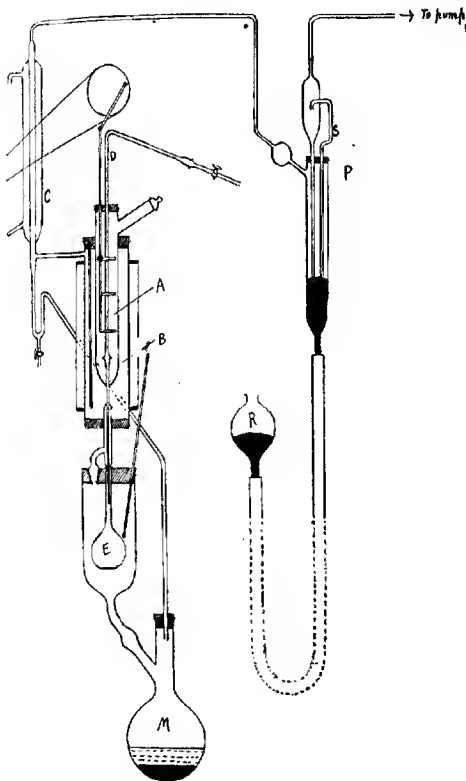
#### *Apparatus.*

As it was necessary to determine the concentration of the solvent in the saturated solution besides the solubility of the solute, the ordinary type of solubility apparatus was not suitable, and a special form had to be devised. This is best explained by reference to Fig. 1.

The solvent with excess of the solute (in not too fine a powder) is placed in the inner tube *A* and well mixed together with a vortically acting stirrer worked by a small motor. The tube *A* is surrounded by a bath of vapour, which circulates through the cylinder *B*, condenses in *C*, and returns to the boiling flask *M*. When the solution is saturated, it is allowed to settle, and the clear solution run out (by raising the tube *D*) into a small graduated flask *E*, which is maintained at the same temperature as the solution in *A*. The temperature of the vapour-bath is varied by changing the pressure under which the liquid in the flask *M* is boiling. For this purpose the top of the condenser *C* is attached to a water pump, and the pressure can be maintained perfectly constant by a manostat *P*. The level of the mercury column in *P* must necessarily remain constant about the end of the tube *S*. The pressure, and consequently the temperature of the bath, can be varied at will by merely raising or lowering the mercury reservoir *R*. The temperature can with care be maintained constant to 0.01°. For this purpose the apparatus must be quite air-tight, the liquid in the boiling flask must not bump (which is entirely prevented by placing in the flask a layer of mercury), and a pure boiling liquid must be used. The density of the saturated solution (and from this the concentration of the solvent can be calculated) is found by weighing the hottle *H* filled up to the graduation on the neck with the saturated solution. The volume of this hottle had previously been

determined with great care, and corrections made for expansion of the glass, curved surface of meniscus, etc. After being weighed, the contents (and washings) of the bottle *E* are poured into a special form of evaporating bottle (Fig. 2). The body of this

FIG. 1.



bottle is immersed in a water-bath kept at a temperature too low for any escape by volatilisation of the dissolved substance, and the evaporation carried out by drawing over the surface a rapid current of dry air.

Two thermometers graduated in fifths of a degree, and readable



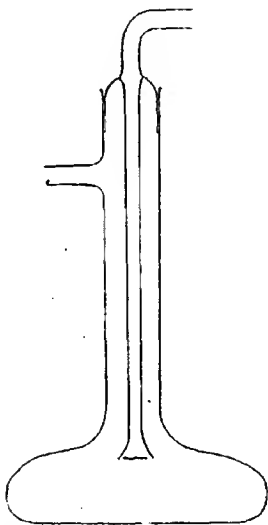
to 1/50th of a degree, were used, one in the lower portion of the apparatus, and the other in the higher portion.

Kahlbaum's chemicals were used without any further purification.

### Results.

The values given in the tables below were read from the smoothed curves of experimental results, which, in the case of the solubility determinations in the pure solvents at varying temperatures, were

FIG. 2.



made every 5° or 6°. The lowest temperatures (10°—13°) were obtained by substituting for the vapour-bath a current of cold water at constant temperature. The results for 0° were obtained by extrapolation, and are probably a little less accurate than the other figures. The probable error in the values given for the solubilities in the pure solvents is about  $\pm 0.001$  to  $\pm 0.002$ , whilst the figures for the concentration of the solvent are accurate to about 0.0002 gram per c.c.

*Solubility of Anthraquinone in Benzene.*

Tem- perature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
0°	0.110	0.8986
10	0.173	0.8890
20	0.256	0.8771
30	0.350	0.8653
40	0.495	0.8543
50	0.700	0.8429
60	0.974	0.8310
70	1.355	0.8180
80	1.775	0.8044

*Solubility of Anthraquinone in Chloroform.*

Tem- perature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
0°	0.340	1.5180
10	0.457	1.4975
20	0.605	1.4765
30	0.780	1.4545
40	0.994	1.4315
50	1.256	1.4086
55	1.415	1.3967
60	1.577	1.3847

*Solubility of Anthracene in Benzene.*

Temperature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
0°	0.605	0.8940
10	0.975	0.8820
20	1.43	0.8686
30	2.03	0.8547
40	2.78	0.8394
50	3.75	0.8234
60	5.14	0.8070
70	7.00	0.7876
75	8.35	0.7772

The values for the solubility in the above table are accurate to the last decimal figure given. They differ rather considerably, however, from values given by Findlay (Trans., 1902, **81**, 1221). Most of Findlay's values were not experimentally determined, but calculated by aid of a theoretical expression enabling the comparison of one solubility curve with another. His results for the higher temperatures are undoubtedly much too low, and those for lower temperatures too high.

*Solubility of Phenanthraquinone in Benzene.*

Tem- perature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
10°	0.412	0.8667
15	0.471	0.8807
20	0.538	0.8750
30	0.788	0.8633
40	1.032	0.8514
50	1.364	0.8390
60	1.780	0.8263
70	2.687	0.8112
80	3.770	0.7950

*Solubility of Phenanthraquinone in Ethyl Acetate.*

Tem- perature.	Solubility in grams per 100 grams of solvent.	Concentration of solvent in grams per c.c.
10°	0.513	0.0092
20	0.626	0.8969
30	0.770	0.8840
40	0.995	0.8707
50	1.292	0.8567
55	1.457	0.8498
60	1.640	0.8423
65	1.902	0.8348
70	2.215	0.8270
75	2.515	0.8188

An interesting point about the above figures is that the concentration of the solvent in the saturated solution is very approximately a linear function of the temperature. For example, the concentration of a saturated solution of phenanthraquinone in benzene is given approximately by the equation:

$$C = 0.8986 - 0.00119t,$$

where  $t$  is the temperature in degrees centigrade. Introducing this approximation into the fundamental equation, we can write:

$$S = K.f(a - bt). \phi(t),$$

where  $a$  and  $b$  are constants. This gives the solubility in terms of the temperature.

*Solubility of Anthraquinone in Chloroform diluted with Hexane at 12.6°.*

The solubility in the hexane alone at 12.6° is 0.006 per cent., and in the chloroform alone 0.482 per cent. This difference is sufficiently great to justify the supposition that the amount dissolved by the hexane alone in the mixture is proportional to the concentration of the hexane. The values of the solubility in the following table have been found by determining the solubility in the mixed solvent and subtracting for the amount dissolved by the hexane alone. The values for the smaller concentrations are only approximate, for the error of the above approximation is here greatest. The solubilities for the concentration of 1.5000 grams per c.c., given in all the chloroform solutions, were found by extrapolation, as the concentration of pure chloroform is below this value.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0.0	0.0	0.9000	0.255
0.1500	0.036	1.0500	0.305
0.3000	0.077	1.2000	0.353
0.4500	0.120	1.3500	0.420
0.6000	0.163	1.5000	0.507
0.7500	0.210		

*Solubility of Anthraquinone in Chloroform diluted with Hexane at 49°*

In this case the solubility in the chloroform alone is about twenty-two times greater than that in the hexane.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0.0	0.0	0.9000	0.730
0.1500	0.123	1.0500	0.857
0.3000	0.241	1.2000	1.000
0.4500	0.363	1.3500	1.144
0.6000	0.483	1.5000	1.297
0.7500	0.608		

*Solubility of Phenanthraquinone in Chloroform diluted with Pentane at 14.5°.*

In this case the solubility in the chloroform alone is about seventy times greater than that in the pentane.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0.500	0.390	1.300	1.920
0.700	0.603	1.400	2.250
0.900	0.885	1.500	2.580
1.100	1.290		

*Solubility of Phenanthraquinone in Benzene diluted with Pentane at 15.5°.*

0.0	0.0	0.500	0.258
0.100	0.037	0.600	0.317
0.200	0.082	0.700	0.375
0.300	0.133	0.800	0.435
0.400	0.195		

*Solubility of Phenanthraquinone in Ethyl Acetate diluted with a Mixture of Hydrocarbons from Petroleum at 48°.*

As a diluent, a mixture of hydrocarbons boiling between 82° and 92°, distilled from petroleum, was used. The solubility in the acetic ester alone is about eighteen times greater than in the mixture of hydrocarbons.

Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of solvent in grams per c.c.	Solubility in grams per 100 of solvent.
0.200	0.617	0.600	1.096
0.300	0.775	0.700	1.173
0.400	0.913	0.800	1.212
0.500	1.015	0.900	1.243

*Solubility of Phenanthraquinone in Benzene diluted with a Mixture of Hydrocarbons from Petroleum at 48°.*

Concentration of benzene in grams per c.c.	Solubility in grams per 100 of solvent.	Concentration of benzene in grams per c.c.	Solubility in grams per 100 of solvent.
0.0	0.0	0.500	0.742
0.100	0.140	0.600	0.888
0.200	0.290	0.700	1.036
0.300	0.440	0.800	1.194
0.400	0.593	0.850	1.300

*Solubility of Benzil in Benzene diluted with Hexane at 12.3°.*

The solubility in the benzene is about fifty times greater than in the hexane.

0.0	0.0	0.500	24.8
0.200	9.0	0.600	32.8
0.300	13.2	0.700	38.9
0.400	18.3		

*Conclusions.*

The results given in the above tables have been plotted graphically (see Fig. 3). The curves given are not all on the same scale, but still they serve to indicate the general form of the relation between the solvent-concentration and the solubility. It will be observed that the cases studied do not give a common type of curve as was at first expected. This means that the law governing the relation between the solubility and the concentration of the solvent is not general, but is dependent on the nature of the substances. Several of the cases do, however, give curves which approximately represent the solubility as a linear function of the concentration of the solvent. In the case of phenanthraquinone in benzene at 48°, for example (curve C), the solubility is given fairly closely by the simple relation,  $S = 1.48C$ , where  $S$  is the solubility and  $C$  the solvent-concentration. Phenanthraquinone in benzene at 15.5°, and anthraquinone in chloroform at 49° and at 12.6° approximate rather less closely to the linear function. The other cases, however, can only be represented accurately by an equation of the form:

$$S = aC + bC^2 + cC^3,$$

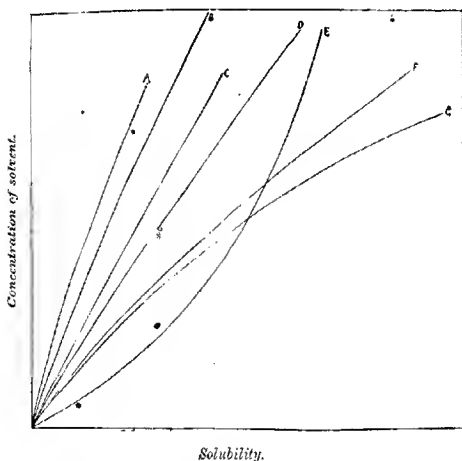
where  $a$ ,  $b$ , and  $c$  are constants.

There is a possibility that in the case of phenanthraquinone in acetic ester (curve E), molecular association occurs, and this would be sufficient to explain the exceptional nature of the curve. In support of this, it may be mentioned that Möller (*Zeitsch. physikal.*

*Chem.*, 1909, **69**, 449) finds that in a mixture of carbon tetrachloride and acetic ester a large proportion of the latter exists as double molecules.

With a mixture of associated solvents, we might expect to obtain very irregular curves through the formation of complex molecules. Holleman and Antusch (*Rec. trav. chim.*, 1894, **13**, 277), working with a mixture of ethyl alcohol and water, and with organic solutes which are much more soluble in the former than in the latter, found

FIG. 3.



- A. Phenanthraquinone in benzene at 15.5° (diluent: pentane).
- B. Anthraquinone in chloroform at 12.6° (diluent: hexane).
- C. Phenanthraquinone in benzene at 48° (diluent: mixture of hydrocarbons).
- D. Anthraquinone in chloroform at 49° (diluent: hexane).
- E. Phenanthraquinone in ethyl acetate at 48° (diluent: hydrocarbons).
- F. Benzil in benzene at 12.3° (diluent: hexane).
- G. Phenanthraquinone in chloroform at 14.5° (diluent: pentane).

in many cases (acetanilide, acetnaphthalide, benzamide, etc.) that the solubility in the mixed solvent, starting from pure alcohol, increased at first as the proportion of the water in the mixture increased, reached a maximum, and then decreased. Herz and Knoch (*Zeitsch. anorg. Chem.*, 1904, **41**, 315) found that succinic acid dissolved in a mixture of acetone and water gave a similar maximum solubility.

The existence of these maxima can only be explained on the supposition that associated molecules are formed with the two solvents which have a greater solvent action on the particular solutes than have the pure solvents.

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### CXC.—A New Method for the Preparation of Aryl Ethers of Glycerol $\alpha$ -Monochlorohydrin.

By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

In the preparation of glycidic aryl ethers by the action of epichlorohydrin on a solution of a phenol in excess of sodium hydroxide (Trans., 1908, **93**, 838; 1909, **95**, 1808), we have invariably observed amongst the products of the reaction a small quantity of a compound containing chlorine, which we assumed to be the glycerol  $\alpha$ -monochlorohydrin aryl ether,  $\text{Ar}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ .

\* This fact led us to investigate whether sodium hydroxide might be advantageously employed as a catalytic agent to bring about the addition of a phenol to epichlorohydrin. We find that this is so. In the presence of a small quantity of sodium hydroxide, epichlorohydrin and phenol react at the ordinary temperature with moderate rapidity to form  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane. From a mixture of 94 grams of phenol and 92.5 grams of epichlorohydrin, to which 0.5 gram of sodium hydroxide had been added, we obtained, after the mixture had been kept for about three weeks, 66 grams of chlorohydrin ether, boiling at  $151\text{--}160^\circ/18$  mm.; from this, on fractionation, 49 grams, boiling at  $155\text{--}156^\circ/16$  mm., were obtained.

Fischer and Krämer (Ber., 1908, **41**, 2728), following the method of Lindemann (Ber., 1891, **24**, 2145), have prepared the phenyl ether ( $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane) by heating epichlorohydrin with phenol in a closed vessel for forty hours at  $160^\circ$ . They give  $152\text{--}153^\circ/12$  mm. as the boiling point of the pure substance. They obtained, from 500 grams of epichlorohydrin and 600 grams of phenol, 173 grams of crude ether, boiling at  $135\text{--}155^\circ/12$  mm.; the yield of the pure compound is not mentioned.

Fourneau (J. Pharm. Chim., 1910, [vii], **1**, 58) gives 25 to 30 grams as the yield of chlorohydrin ether obtained from 65 grams of phenol by the same method, but no boiling point is mentioned.

Fourneau (*loc. cit.*) has also prepared  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane by boiling phenol with a large excess of epichlorohydrin. The yield mentioned is 20 to 22 grams from 35 grams of phenol, but no information is given with regard to the purity of this product. The boiling point given by Fourneau for the pure substance,  $170^{\circ}/21$  mm., appears to be considerably too high.

Using Lindemann's method, and heating for ten hours at  $150^{\circ}$ , we have obtained about 5 grams of  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane, boiling at  $152$ — $155^{\circ}/12$  mm., from 47 grams of phenol. We were unable to detect the presence of any phenyl glycid ether, which, according to Lindemann, is one of the products formed when epichlorohydrin is heated with phenol.

#### EXPERIMENTAL

##### $\gamma$ -Chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane, $C_6H_5 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$ .

Half a gram of sodium hydroxide ( $1/80$  mol.), dissolved in about 5 c.c. of water, was added to a mixture of 94 grams of phenol (1 mol.) and 92.5 grams of epichlorohydrin (1 mol.). The mixture formed a clear solution. After it had been kept for about three weeks at the laboratory temperature, it had still a strongly alkaline reaction. It was then treated with ether; the ethereal solution was shaken with dilute sodium hydroxide solution to remove unchanged phenol, and dried over potassium carbonate. On distillation of the product under diminished pressure, 66 grams of  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane, boiling at  $151$ — $160^{\circ}/18$  mm., were obtained. The residue in the distilling flask was very small in amount. Fractional distillation of the crude ether gave 49 grams of oil, boiling at  $155$ — $156^{\circ}/16$  mm. The portion analysed boiled at  $156^{\circ}/16$  mm. (Found,  $C=57.90$ ;  $H=6.11$ ;  $Cl=18.85$ . Calc.,  $C=57.89$ ;  $H=5.94$ ;  $Cl=19.01$  per cent.) Prepared in this way, the ether forms a colourless, somewhat viscous oil, with a scarcely noticeable odour. On treatment with solid potassium hydroxide, it is converted into phenyl glycid ether.

The *phenylurethane*,  $C_6H_5 \cdot O \cdot CH_2 \cdot CH(O \cdot CO \cdot NH \cdot C_6H_5) \cdot CH_2Cl$ , was prepared by keeping a mixture of the chlorohydrin ether and phenyl isocyanate for twelve days at the ordinary temperature. The solid mass obtained was treated with warm alcohol. The alcoholic solution was filtered, and the *phenylurethane*, obtained on evaporation of the alcohol, was crystallised several times from light petroleum. It forms needles, melting at  $70^{\circ}$ :

0.2351 gave 0.1111 AgCl.  $Cl=11.69$ .

0.4131 " 16.65 c.c.  $N_2$  (moist) at  $20^{\circ}$  and 740 mm.  $N=4.49$ .

$C_{16}H_{16}O_3NCl$  requires  $Cl=11.60$ ;  $N=4.58$  per cent.



*$\gamma$ -Chloro- $\beta$ -hydroxy- $\alpha$ -tolylloxypropane,*  
 $C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$ .

This substance was prepared by the same method as that employed for the phenyl ether. Fifty-four grams of *o*-cresol (1 mol.), 46 grams of epichlorohydrin (1 mol.), and 0.5 gram of sodium hydroxide (1/40 mol.) were used. After nine days the mixture was still strongly alkaline. The yield of crude substance, boiling at 169–172°/22 mm., was 25 grams. The pure ether forms a colourless, somewhat viscous oil, boiling at 166°/18 mm.:

0.2278 gave 0.1627 AgCl. Cl=17.67.

$C_{10}H_{13}O_2Cl$  requires Cl=17.68 per cent.

The *phenylurethane*,  $C_7H_7 \cdot O \cdot CH_2 \cdot CH(O \cdot CO \cdot NH \cdot C_6H_5) \cdot CH_2Cl$ , prepared as in the previous case, crystallised from a solution in cold alcohol, on addition of a little water, in needles, melting at 81–82°:

0.2715 gave 0.1203 AgCl. Cl=10.96.

0.2843 „ 10.9 c.c.  $N_2$  (moist) at 20° and 744 mm. N=4.29.

$C_{17}H_{18}O_3NCl$  requires Cl=11.09; N=4.38 per cent.

*$\gamma$ -Chloro- $\beta$ -hydroxy- $\alpha$ -*p*-tolylloxypropane,*  
 $C_7H_7 \cdot O \cdot CH_2 \cdot CH(OH) \cdot CH_2Cl$ .

Fifty-seven grams of *p*-cresol, 46 grams of epichlorohydrin, and 1 gram of sodium hydroxide were used, and the mixture was kept for eight days. The yield of crude substance, boiling at 178–183°/30 mm., was 47.5 grams. The pure ether boils at 165°/14 mm., and forms a colourless, rather viscous oil:

0.2036 gave 0.1447 AgCl. Cl=17.58.

$C_{10}H_{13}O_2Cl$  requires Cl=17.68 per cent.

The *phenylurethane*,  $C_7H_7 \cdot O \cdot CH_2 \cdot CH(O \cdot CO \cdot NH \cdot C_6H_5) \cdot CH_2Cl$ , prepared as in the previous cases, crystallised from alcohol in needles, melting at 113–114°:

0.2349 gave 0.1051 AgCl. Cl=11.06.

0.3017 „ 11.6 c.c.  $N_2$  (moist) at 17.5° and 751 mm. N=4.40.

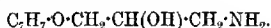
$C_{17}H_{18}O_3NCl$  requires Cl=11.09; N=4.38 per cent.

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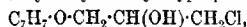
CXCI.—*The Action of Ammonia on the Glycidic Aryl Ethers. Part II. Phenoxypropanolamines.*

By DAVID RUNCIMAN BOYD.

IN a previous communication (Boyd and Knowlton, *Trans.*, 1909, 95, 1802) an account was given of the bases obtained by the action of ammonia on *o*-tolyl glycidic ether. From analogy to other cases, it was considered probable that in this reaction the amino-group becomes attached to the  $\alpha$ -carbon atom of the *o*-tolyl glycidic ether, giving a primary base of the formula



This view has now been confirmed by the preparation of the same base from  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -o-tolyloxypropane,

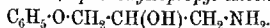


and ammonia.

The action of ammonia on phenyl glycidic ether has also been studied, and bases similar in character to those resulting from *o*-tolyl glycidic ether have been obtained.

This reaction has also been investigated recently by Fournneau, who states (*J. Pharm. Chim.*, 1910, [vii], 1, 99) that phenyl glycidic ether and  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane react with ammonia to produce a secondary base only, and who appears to regard such behaviour as typical of the aromatic and higher fatty halogen-hydrins. It is obvious, however, that the relative quantities of primary, secondary, and tertiary bases obtained in such a reaction as that under consideration must depend very largely on the conditions of the experiment. If, for instance, the glycidic ether is dissolved in a considerable volume of a strong solution of ammonia in 50 per cent. alcohol, the principal product is the primary base.

## EXPERIMENTAL.

 *$\beta$ -Amino- $\beta'$ -phenoxyisopropyl Alcohol,*

The hydrochloride of this base was prepared by the method already described in connexion with the corresponding *o*-tolyloxy-compound (*loc. cit.*). In one experiment, using 38 grams of phenyl glycidic ether, 200 c.c. of concentrated aqueous ammonia, and 180 c.c. of alcohol, and keeping the mixture for some days at the ordinary temperature, about 30 grams of the hydrochloride were obtained. The salt resembles the corresponding *o*-tolyloxy-com-

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compound in having no definite melting point. It softens at  $136^{\circ}$ , but is not completely melted until about  $228^{\circ}$ . It dissolves very easily in cold water.

The free base separated in rosettes of small needles on adding sodium hydroxide to a concentrated aqueous solution of the hydrochloride. After washing with water and drying in a desiccator over potassium hydroxide, it melted at  $97-98^{\circ}$ :

0.1727 gave 0.4092  $\text{CO}_2$  and 0.1204  $\text{H}_2\text{O}$ .  $\text{C}=64.62$ ;  $\text{H}=7.81$ .

0.1932 „ 14.2 c.c.  $\text{N}_2$  (moist) at  $12^{\circ}$  and 761 mm.  $\text{N}=8.52$ .

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}$  requires  $\text{C}=64.62$ ;  $\text{H}=7.85$ ;  $\text{N}=8.38$  per cent.

The base is easily soluble in water, giving a solution with a strongly alkaline reaction; it is less soluble in water containing sodium hydroxide.

The *platinichloride* melts and decomposes at  $201^{\circ}$ :

0.3066 gave 0.0804 Pt. Pt=26.22.

$(\text{C}_8\text{H}_{13}\text{O}_2\text{N})_2\text{H}_2\text{PtCl}_6$  requires Pt=26.21 per cent.

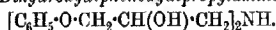
The *benzoate* crystallises from alcohol in prisms, which soften at  $140^{\circ}$ , and melt at  $143^{\circ}$ :

0.2560 gave 10.9 c.c.  $\text{N}_2$  (moist) at  $17^{\circ}$  and 747 mm.  $\text{N}=4.82$ .

$\text{C}_8\text{H}_{13}\text{O}_2\text{N}\cdot\text{C}_6\text{H}_5\text{O}_2$  requires  $\text{N}=4.84$  per cent.

$\beta$ -Amino- $\beta'$ -phenoxyisopropyl alcohol can also be prepared by treating  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane with a solution of ammonia in 50 per cent. alcohol. The method of procedure is practically the same as when the glycidic ether is employed, except that after the alcohol and ammonia have been expelled, it is necessary to add some dilute hydrochloric acid in order to precipitate the hydrochloride of the secondary base, which otherwise would remain to some extent in solution along with the salt of the primary amine.

*Dihydroxydiphenoxydipropylamine,*



A secondary base, melting at  $97-98^{\circ}$ , and giving a hydrochloride melting at  $175^{\circ}$ , has been described by Fournau (*loc. cit.*) as the product obtained by heating  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -phenoxypropane with aqueous ammonia.

The crude product obtained from phenyl glycidic ether and ammonia, which melted about  $97^{\circ}$ , was washed twice with ether, and then treated with hydrochloric acid. After several crystallisations from dilute alcohol, the hydrochloride softened at  $169^{\circ}$ , and melted at  $171-172^{\circ}$ . (Found,  $\text{Cl}=9.89$ . Calc.,  $\text{Cl}=10.03$  per cent.) The salt is moderately soluble in cold water, but only very sparingly so in water containing hydrochloric acid.

The free base was obtained by adding sodium hydroxide to a

solution of the hydrochloride in boiling dilute alcohol. After two crystallisations from alcohol, it melted almost completely at  $101-102^{\circ}$ , but fusion was not quite complete until  $104^{\circ}$ . Since the nitrogen estimation gave a result in satisfactory agreement with the figure required for a secondary base, it seems possible that the want of sharpness in the melting point may be due to the presence of both of the two possible stereoisomerides. (Found, N=4.46. Calc., N=4.42 per cent.)

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### CXCH.—*The Resolution of Benzoyloscine.*

By FRANK TUTIN.

THE base oscine (scopoline),  $C_8H_{13}O_2N$ , formed by the hydrolysis of the alkaloid hyoscyne (scopolamine), is generally acknowledged to be closely related structurally to tropine,  $C_8H_{13}ON$ , although its constitution is not known. Tropine, which contains two similar asymmetric carbon atoms, has recently been examined from a stereochemical point of view by M. Barrowcliff and the present author (Trans., 1909, 95, 1966), and found to be an internally compensated compound. It was therefore considered of interest to investigate oscine in the same direction, particularly as the evidence so obtained might be of service in assigning a constitutional formula to this compound.

Oscine was prepared from *l*-hyoscyne, and examined polarimetrically, when it was found to be optically inactive. As the amount of material prepared was not large, the base was converted into its benzoyl derivative before attempting its resolution, thereby increasing the size of the molecule. Moreover, the salts of benzoyloscine crystallise more readily than those of the original base.

*Benzoyloscine d-camphorsulphonate* (m. p.  $167-168^{\circ}$ ) was first prepared, but, although this salt was submitted to a prolonged fractional crystallisation, no evidence of resolution could be obtained. When, however, *benzoyloscine d-bromocamphorsulphonate* was fractionally crystallised, it was at once seen that a separation was being effected, and, after three fractionations, *benzoyl-d-oscline d-bromocamphorsulphonate* (m. p.  $246^{\circ}$ ) was obtained in a state of purity. This salt had  $[\alpha]_D +51.9^{\circ}$  in aqueous solution, from which it is calculated that the basic ion has  $[\alpha]_D +10.0^{\circ}$ . The base obtained from this salt, when examined in 50 per cent. alcohol, had

$[\alpha]_D + 3.5^\circ$ . In order further to characterise this optically active base, several salts were prepared from it, each of which was found to melt at a higher temperature than the corresponding salt of the inactive base, as will be seen from the following table:

Name of salt	M. p. of salt of <i>d</i> -base.	M. p. of salt of <i>d</i> -base.
Hydrochloride .....	266*	283—284*
Nitrate .....	195	200*
Picrate .....	185	211—212
Aurichloride .....	183—194	180—190

*d*-Oscine could not be obtained from benzoyl-*d*-oscine by hydrolysis with an alkali, since racemisation rapidly occurred under these conditions. Recourse was therefore had to acid hydrolysis, the liberated benzoic acid being removed by means of steam. A solution containing *d*-oscine hydrochloride was thus obtained, by means of which an approximate determination of the optical rotatory power of *d*-oscine was made, when the value  $[\alpha]_D + 77.7^\circ$  was found.

Attempts to obtain benzoyl-*l*-oscine *d*-bromocamphorsulphonate in a state of purity were unsuccessful.

It is evident from the results given in this paper that oscine is capable of resolution into two stereoisomerides, and no evidence of the existence of more than two such compounds was obtained. Any structural formula which may be assigned to this base must therefore contain either one or two asymmetric carbon atoms, but, if the latter be the case, both the asymmetric groupings must be similar.

#### EXPERIMENTAL.

About five grams of *l*-hyoscine (scopolamine) were heated for several hours on a water-bath with a large excess of alcoholic potassium hydroxide. Water was then added, and the resulting oscine (scopoline) extracted with chloroform, after which it was purified by distillation, when it passed over at 240—245°. The solid so obtained, which was optically inactive, was treated with a large excess of benzoyl chloride, when an additive compound of the base and the acid chloride was first formed. On heating the mixture, however, this substance dissolved, and then the liquid darkened somewhat, after which benzoyleoscine hydrochloride separated in almost quantitative yield, the mixture becoming solid. After allowing the reaction mixture to cool, it was crushed in a mortar and mixed with ether, the solid being collected, and washed with this solvent. On recrystallisation from alcohol, the benzoyleoscine hydrochloride was obtained in tufts of colourless needles, which melted and evolved gas at 266°. This melting point is higher than that previously given for the salt in question, namely, 249—250° (*Beilstein's Handbuch, Ergänzungsband, III, p. 619*).

and in order, therefore, to confirm the identity of the product, it was converted into the aurichloride. This salt crystallised in small tufts of yellow needles and melted at 183—184°:

0.0864 gave 0.0284 Au.  $\text{Au} = 32.9$ .

$\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}, \text{HAuCl}_4$  requires  $\text{Au} = 33.0$  per cent.

Benzoyloscine nitrate, prepared from the above-described hydrochloride, was very sparingly soluble in water, from which it crystallised in long, colourless needles. It melted and violently evolved gas at 195°. The corresponding picrate crystallised well in flattened needles, and melted at 185° without decomposing.

Benzoyloscine (benzoylscopoline) has previously been prepared by the repeated evaporation of oscine benzoate with dilute hydrochloric acid (D.R.-P. 79864), but the above-described method is far more expeditious, and gives much better yields.

#### *Benzoyloscine d-Camphorsulphonate.*

The benzoyloscine obtained from the above-described hydrochloride was converted into its *d-camphorsulphonate*. This salt was dissolved in ethyl acetate containing a little alcohol, when, after some time, it separated in the form of a white powder. When examined under the microscope, this was seen to consist of minute, diamond-shaped crystals.

*Benzoyloscine d-camphorsulphonate* melted at 167—168°, but, although it was submitted to a prolonged fractional crystallisation, no evidence of resolution could be obtained:

0.1476 gave 0.3312  $\text{CO}_2$  and 0.0918  $\text{H}_2\text{O}$ .  $\text{C} = 61.2$ ;  $\text{H} = 6.9$ .

$\text{C}_{15}\text{H}_{17}\text{O}_3\text{N}, \text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$  requires  $\text{C} = 61.1$ ;  $\text{H} = 6.7$  per cent.

0.4226, made up to 20 c.c. with water, gave  $\alpha_D + 0.26'$  in a 2-dm. tube, whence  $[\alpha]_D + 10.3^\circ$ ;  $[\text{M}]_D + 50.6^\circ$ .

#### *Resolution of Benzoyloscine d-Bromocamphorsulphonate.*

The base was recovered from the previously-described *d-camphorsulphonate*, and neutralised with *d-bromocamphorsulphonic acid*. The salt so obtained crystallised fairly readily from water, but much more easily from a mixture of ethyl acetate and alcohol, forming colourless needles. After one recrystallisation, it had somewhat the appearance of a mixture, and melted at 234—239°, previously softening at 211°.

0.4068, made up to 20 c.c. with water, gave  $\alpha_D + 2.2'$  in a 2-dm. tube, whence  $[\alpha]_D + 50.0^\circ$ ;  $[\text{M}]_D + 285.0^\circ$ .

Since *d-bromocamphorsulphonic acid* has  $[\text{M}]_D + 271^\circ$ , it appeared that the benzoyloscine *d-bromocamphorsulphonate* was resolving.

It was again crystallised as before, when it seemed much less soluble, and melted at 238–244°.

0.3982, made up to 20 c.c. with water, gave  $\alpha_D + 2.4^\circ$  in a 2-dcm. tube, whence  $[\alpha]_D + 51.9^\circ$ ;  $[M]_D + 295.8^\circ$ .

When recrystallised a third time, this salt yielded handsome, glistening needles, which melted sharply at 246–246.5°.

0.4092, made up to 20 c.c. with water, gave  $\alpha_D + 2.8^\circ$  in a 2-dcm. tube, whence  $[\alpha]_D + 52.1^\circ$ ;  $[M]_D + 297.0^\circ$ .

This salt was evidently that of the dextrorotatory component of the racemic base, and since, as shown below, it yielded *d*-oscine on hydrolysis, it must be designated *benzoyl-d*-oscine *d*-bromocamphorsulphonate. Repeated crystallisation caused no further change in its melting point or rotatory power:

0.1437 gave 0.2767 CO<sub>2</sub> and 0.0800 H<sub>2</sub>O. C=52.5; H=6.2.

C<sub>13</sub>H<sub>17</sub>O<sub>3</sub>N, C<sub>10</sub>H<sub>15</sub>O<sub>4</sub>BrS requires C=52.6; H=5.7 per cent.

The molecular rotation of *benzoyl-d*-oscine, calculated from that of its *d*-bromocamphorsulphonate, is  $[M]_D + 26.0^\circ$ , whence the basic ion has  $[\alpha]_D + 10.0^\circ$ .

A small quantity of the above-described salt of *benzoyl-d*-oscine was treated with sodium carbonate, the base extracted with chloroform, and examined polarimetrically, when a reading of  $+0.25^\circ$  was obtained. It was evident, therefore, that the base could be obtained in the free state without suffering complete racemisation. A larger quantity of the salt was then decomposed, and the resulting base dissolved in 20 c.c. of 50 per cent. alcohol, when it had  $\alpha_D + 0.49^\circ$  in a 2-dcm. tube. Ten c.c. of the solution were subsequently found, on titration, to contain 0.1172 of base, whence  $[\alpha]_D + 3.5^\circ$ ;  $[M]_D + 9.75^\circ$ . The fact that the value thus obtained for the rotation of *benzoyl-d*-oscine is lower than that previously calculated for the basic ion of *benzoyl-d*-oscine *d*-bromocamphorsulphonate ( $[\alpha]_D + 10.0^\circ$ ) may be due, in part, to racemisation, but it is probably largely owing to the fact that the free base is incompletely ionised when dissolved in 50 per cent. alcohol (compare Carr and Reynolds, this vol., p. 1328).

Attempts were made to isolate *benzoyl-l*-oscine *d*-bromocamphorsulphonate, but without success. A fraction of salt, melting at 219–227°, was, however, obtained, the basic ion of which had  $[M]_D - 4.7^\circ$ .

*Benzo**yl-d*-oscine hydrochloride was prepared from the corresponding *d*-bromocamphorsulphonate by double decomposition. It formed colourless needles, melting at 283–284°.

*Benzo**yl-d*-oscine nitrate was similarly prepared. It was very sparingly soluble in water, and crystallised in irregular prisms.

which decomposed violently at 200°, and differed considerably in appearance from the long needles of the corresponding salt of the inactive base.

*Benzoyl-d-oscine picrate* crystallised very readily in handsome, yellow needles, which melted at 211–212° without undergoing any decomposition, a behaviour very remarkable in a picrate melting at so high a temperature.

*Benzoyl-d-oscine aurichloride* crystallised much more readily than the corresponding salt of the inactive base. It formed yellow needles, melting at 189–190°.

#### *Hydrolysis of Benzoyl-d-oscine. Formation of d-Oscine.*

The quantity of base which was employed, as above described, for determining the rotatory power of benzoyl-d-oscine in 50 per cent. alcohol was hydrolysed by means of hydrochloric acid, steam being passed through the mixture for the removal of the benzoic acid formed. To ensure that this was thoroughly accomplished, the operation was continued for three days. The liquid was maintained at a practically constant volume, and examined polarimetrically from time to time, when it was observed that the optical rotation increased appreciably as the hydrolysis proceeded. When the change was complete, the mixture was made alkaline, and the resulting d-oscine rapidly extracted with chloroform. The chloroformic liquids were then concentrated somewhat, and extracted with hydrochloric acid, after which the acid liquid, which measured 23 c.c., had  $\alpha_D + 1^\circ 35'$  in a 2-dcm. tube, whence the specific rotation of d-oscine is calculated at  $[\alpha]_D + 77.7^\circ$ . This result must, however, be regarded as only approximate.

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### CXCIII.—*Note on the Constitution of $\alpha$ -Elaterin.*

By CHARLES WATSON MOORE.

UNDER the title of "elaterin," the British and United States Pharmacopœias recognise a crystalline principle obtained from elaterium—a sediment from the juice of the fruit of *Ecballium Elaterium*, A. Richard.

It has been shown by Power and Moore (*Pharm. J.*, 1909, [iv], 29, 501) that elaterin consists of a mixture of two crystalline



substances of apparently identical percentage composition, but having optical rotations of opposite sign, and which those authors have designated as  $\alpha$ - and  $\beta$ -elaterin (Trans., 1909, 95, 1985). Of these two substances, only the dextrorotatory,  $\beta$ -elaterin, possesses physiological activity, the levorotatory,  $\alpha$ -elaterin, which is the principal constituent of the elaterin of commerce, being quite inert.

Berg (*Bull. Soc. chim.*, 1897, [iii], 17, 85) has stated that elaterin does not exist as such in the fruit of *Ecballium Elaterium*, but that it is formed, after the expression of the juice, by the action of an enzyme on an amorphous glucoside. This view is not in agreement with the results obtained by Power and Moore (Trans., 1909, 95, 1985), it having been definitely established by those authors that no glucoside of elaterin was present in the fruit of *Ecballium Elaterium*. Recently, Berg (*Bull. Soc. chim.*, 1910, [iv], 7, 385), in support of his earlier view, has described the characters of the so-called "glucoside" of elaterin, and recorded an analysis of it. This "glucoside" is, however, an amorphous, indefinite product, evidently consisting of a mixture of substances, and any deductions made from the analysis of such material with respect to its composition have little or no value. The present author therefore, with the concurrence of Dr. F. B. Power, sees no reason to depart from the view previously expressed (*loc. cit.*), that elaterin is not present in the form of a glucoside in the fruit of *Ecballium Elaterium*.

It has quite recently been shown by Power and Moore (this vol., p. 99) that  $\alpha$ -elaterin likewise occurs in the fruit of *Citrullus Colocynthis*, Schrader, and the material employed in the present investigation was obtained from this source.

During the last few years elaterin has been the subject of a considerable number of investigations, and, while the presence of certain groups in the molecule has been established, there is still divergence of opinion among the different investigators as to the empirical formula of the substance.

The formula adopted for elaterin by the Pharmacopœias, namely,  $C_{20}H_{28}O_5$ , is that put forward by Zwenger (*Annalen*, 1842, 43, 460), but more recently Berg (*Bull. Soc. chim.*, 1905, [iii], 35, 435), Hemmelmayr (*Ber.*, 1906, 39, 3652), and Thoms (*Apoth. Zeit.*, 1906, 21, 803) have suggested different empirical formulae, namely,  $C_{23}H_{38}O_7$ ,  $C_{24}H_{34}O_6$ , and  $C_{25}H_{30}O_6$  respectively.

Of these formulae, that indicated by Thoms (*loc. cit.*) is not in agreement with the analytical results obtained by all other investigators, while those of Zwenger, Berg, and Hemmelmayr require almost identical percentages of carbon and hydrogen, as follows:

$C_{20}H_{28}O_5$ (Zwenger)	requires	C=68.9; H=8.0	per cent.
$C_{23}H_{36}O_7$ (Berg)	"	C=69.1; H=7.8	"
$C_{24}H_{34}O_6$ (Hemmelmayer)	"	C=68.9; H=8.0	"
$C_{22}H_{30}O_6$ (Thoms)	"	C=67.7; H=7.7	"

Owing to the slight solubility of elaterin in most solvents, molecular-weight determinations of this substance by means of the cryoscopic or the ebullioscopic methods are not trustworthy, and different results have been obtained by various investigators. Thus, Pollak (*Ber.*, 1906, **39**, 3380) obtained results in agreement with Berg's formula by means of the cryoscopic method, using phenol as solvent, whilst by the employment of the ebullioscopic method, using ethylene bromide as solvent, he obtained figures more in agreement with the formula of Zwenger and Thoms. Power and Moore (*Pharm. J.*, 1909, [iv], **29**, 501), on the other hand, have obtained results in agreement with the formula of Berg by means of the ebullioscopic method, using chloroform as solvent.

It is necessary, therefore, to have recourse to chemical methods to establish the molecular weight of this substance, but as all the hitherto described derivatives and decomposition products of elaterin are indefinite and amorphous, no satisfactory conclusions can be arrived at regarding their empirical formulae.

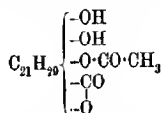
It has been shown by Berg (*Bull. Soc. chim.*, 1905, [iii], **35**, 435) that when elaterin is treated for a short time with alcoholic sodium hydroxide, one molecule of acetic acid is split off, an amorphous, phenolic substance, "elateridin," being formed. Elaterin therefore appears to contain an acetyl group, and the estimation of the acetic acid formed by its hydrolysis affords evidence in support of Berg's formula.

Elaterin appears also to contain a lactone grouping, as by the prolonged action of boiling sodium hydroxide solution it is converted into "elateric acid," which, like "elateridin," is an amorphous product (Berg, *Bull. Soc. chim.*, 1905, [iii], **35**, 435; *Compt. rend.*, 1909, **148**, 1679). Thoms (*loc. cit.*) assumes the presence of two lactone groupings in elaterin, whilst Hemmelmayer (*loc. cit.*) explains the formation of "elateric acid" as being due to the oxidation of an aldehyde group. The latter explanation, however, does not appear to be tenable, for, although Hemmelmayer (*loc. cit.*) describes the preparation of a dihydrazone of elaterin (see also Berg, *Compt. rend.*, 1906, **143**, 1161), the present author has been unable to obtain any evidence as to the presence of a carbonyl group. The "hydrazone" described by Hemmelmayer is an amorphous, indefinite product, and there is no evidence that it is not a phenylhydrazide. Moreover, as such a compound would be obtained by the action of phenylhydrazine on a lactone grouping,

this appears to be the most likely explanation of the nature of the product.

On heating elaterin with acetic anhydride, a diacetyl derivative is formed (Berg, *Bull. Soc. chim.*, 1906, [iii], 35, 435; Hemmelmayr *Ber.*, 1906, 39, 3653). Elaterin must therefore contain two hydroxyl groups.

If it be assumed that the empirical formula put forward by Hemmelmayr is correct,  $\alpha$ -elaterin might be written as follows:

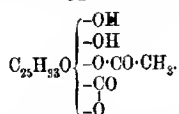


On the other hand, if the empirical formula of Berg be adopted there remains the state of combination of one oxygen atom to account for.

The present author has now been able to show that by the oxidation of "elateric acid" a definite, crystalline diketone is formed, which possesses the empirical formula,  $\text{C}_{24}\text{H}_{30}\text{O}_2$ , and may be designated *elaterone*.

As "elateric acid" is an indefinite, amorphous product, views as to its constitution, or even its empirical formula, based on analysis are of little or no value. It may, however, safely be assumed that it contains at least two carbon atoms less than elaterin, owing to the removal of the acetyl group from that substance in the course of its formation. As elaterone has now been shown to contain twenty four carbon atoms, it follows that elaterin must contain at least twenty-six, and accordingly, to bring its formula into harmony with the analytical results, this must be written as  $\text{C}_{26}\text{H}_{38}\text{O}_7$ , in agreement with the formula of Berg.

In the present state of our knowledge, therefore, the formula of  $\alpha$ -elaterin may be written as shown below, the manner of combination of one of the seven oxygen atoms being unknown:



It is probable that the oxygen atom above referred to is present in the form of an ether linking, although, as has been shown by Pollak (*Ber.*, 1906, 39, 3880), no methoxyl or ethoxyl group is present.

It has been shown by Thoms (*loc. cit.*) that elaterin is very probably a derivative of naphthalene, since by oxidising elaterin,

and distilling the product with zinc dust, he obtained  $\alpha$ -methyl-naphthalene. The present author, however, by the distillation of elaterin itself with zinc dust, has obtained 1:4-dimethylnaphthalene.

#### EXPERIMENTAL.

The  $\alpha$ -elaterin employed in the present investigation was obtained from Turkish colocynth, consisting of the dried, peeled fruit of *Citrullus Colocynthis*, Schrader, as described by Power and Moore (this vol., p. 99).

As already stated by those authors (*loc. cit.*),  $\alpha$ -elaterin forms colourless, hexagonal prisms, melting and decomposing at  $232^\circ$ , and has  $[\alpha]_D -68.9^\circ$  in chloroform solution (compare Berg, *Compt. rend.*, 1910, 150, 981). On analysis, it gave results agreeing with those found by most other investigators for elaterin. (Found, C=68.9; H=8.1.)

A determination of the iodine value, by Hübl's method, gave the following result:

0.5010 absorbed 0.2673 iodine. Iodine value=53.3.

$C_{25}H_{32}O_7$ , containing one double linking, requires iodine value=52.2.

$\alpha$ -Elaterin is insolub<sup>y</sup> in cold aqueous sodium or potassium hydroxide, but if it is suspended in a small quantity of alcohol, and potassium hydroxide (1 molecule) added to this mixture, the  $\alpha$ -elaterin rapidly dissolves, and is not precipitated on pouring the alcoholic solution into twice its volume of water. On acidification, however, unchanged  $\alpha$ -elaterin is precipitated. Hence it appears that  $\alpha$ -elaterin possesses phenolic properties, and is capable of forming a potassium derivative soluble in alcohol. Attempts to isolate this potassium derivative were, however, unsuccessful, for on keeping the alcoholic solution, even in the cold, hydrolysis occurred with the formation of "elateridin." Attempts to prepare the corresponding methyl derivative by means of sodium ethoxide and methyl iodide were also unsuccessful.

With consideration of the statements of Berg and Hemmelmayer that elaterin contains a carbonyl group (*loc. cit.*), attempts were made to prepare a hydrazone and an oxime. An alcoholic solution of  $\alpha$ -elaterin was boiled for about one hour with phenylhydrazine (1 molecule), but only resinous products resulted. Two experiments were accordingly made at the ordinary temperature. In both cases 1 gram of  $\alpha$ -elaterin was dissolved in 100 c.c. of alcohol, and in one experiment 0.25 gram of phenylhydrazine was added to the solution, whilst in the second experiment, 0.5 gram of phenylhydrazine was used. The solutions were kept at the ordinary temperature for some hours, and were then diluted with water, when in both cases quantities of a yellow, resinous precipitate were

produced. These precipitates were collected, and attempts were made to crystallise them from various solvents. In both cases small quantities of unchanged  $\alpha$ -elaterin were recovered, but there was no indication of the formation of a definite hydrazone. Similar results were obtained on attempting to prepare an oxime. On boiling the alcoholic solution of  $\alpha$ -elaterin with hydroxylamine, there was some decomposition, but when the experiment was conducted at the ordinary temperature (kept twenty-four hours), over 80 per cent. of the  $\alpha$ -elaterin was recovered unchanged.

A quantity (10 grams) of  $\alpha$ -elaterin was distilled, in small quantities at a time, with zinc dust in a current of hydrogen, when a small amount of an oily liquid, possessing a strong naphthalene-like odour, was formed. This was purified by distillation in a current of steam, but as the quantity of volatile substance so obtained was very small, it was converted into its picrate for identification. This crystallised from alcohol in small, orange-coloured needles, melting at  $139^{\circ}$ , and agreed in all respects with the picrate of 1:4-dimethylnaphthalene.

#### *Alkaline Hydrolysis of $\alpha$ -Elaterin.*

It has been shown by Berg (*loc. cit.*) that elaterin is hydrolysed by alkali hydroxides with formation of one molecule of acetic acid and either "elateridin" or "elateric acid," according to the extent of the hydrolysis. A determination of the acetic acid formed in this reaction was made as follows:

Twenty grams of  $\alpha$ -elaterin were boiled for five hours with an excess of aqueous sodium hydroxide. The alkaline solution was then acidified with sulphuric acid, and the volatile acids removed by a current of steam. The acid distillate was found to consist of a mixture of acetic and formic acids.

The total volatile acids neutralised 1.791 grams NaOH, and the amount of formic acid was found to be equivalent to 0.151 gram NaOH. Hence the acetic acid was 2.460 grams = 12.3 per cent.:

$C_{26}H_{35}O_5 \cdot O(CO \cdot CH_3)$  requires acetic acid = 12.3 per cent

#### *Oxidation of "Elateric Acid."*

##### (1) *Formation of Elaterone, $C_{24}H_{30}O_5$ .*

The "elateric acid" was prepared by the action of potassium hydroxide on  $\alpha$ -elaterin, according to the method already described by Berg (*loc. cit.*). It forms a light brown, amorphous powder, soluble in sodium hydrogen carbonate, and appears to contain a carboxyl group. Neither the acid, nor any of its salts, has been obtained in a crystalline state. A determination of its specific rotatory power gave the following result:

MOORE: NOTE ON THE CONSTITUTION OF *a*-ELATERIN. 1803

0.3200, made up to 20 c.c. with ethyl acetate, gave  $\alpha_D + 4.6'$  in a 1 dm. tube, whence  $[\alpha]_D + 23.9^\circ$ .

Ten grams of "elateric acid" were dissolved in 100 grams of glacial acetic acid, and 10 grams of chromic acid, dissolved in 12 grams of water, added, after which the solution was heated on a water-bath. A vigorous reaction occurred, and the liquid boiled spontaneously for some minutes. The mixture was subsequently heated for one hour; then poured into water, and, after the addition of sulphuric acid, it was extracted with chloroform. The chloroform extracts were shaken with aqueous sodium carbonate, which, however, only removed small quantities of resinous material. The chloroform solution was accordingly dried, and the solvent removed, when a quantity of a crystalline substance was obtained. This was recrystallised from boiling alcohol, when it formed long, colourless needles, melting at about  $300^\circ$ . The quantity so obtained amounted to 1.4 grams:

0.1135 gave 0.3000  $\text{CO}_2$  and 0.0805  $\text{H}_2\text{O}$ .  $\text{C} = 72.1$ ;  $\text{H} = 7.9$ .

After recrystallising from alcohol it was again analysed:

0.1390 gave 0.3680  $\text{CO}_2$  and 0.0974  $\text{H}_2\text{O}$ .  $\text{C} = 72.2$ ;  $\text{H} = 7.8$ .

$\text{C}_{24}\text{H}_{30}\text{O}_5$  requires  $\text{C} = 72.4$ ;  $\text{H} = 7.5$  per cent.

The molecular weight of the substance was determined by the cryoscopic method in benzene solution:

0.2616, in 22.34 c.c. benzene, gave  $\Delta t = -0.154^\circ$ . M.W. = 380.

$\text{C}_{24}\text{H}_{30}\text{O}_5$  requires M.W. = 398.

As this substance does not agree in its properties with any compound of this formula which has hitherto been described, it is proposed to designate it *elaterone*, with consideration of the fact that it is a ketone (see below).

Elaterone is sparingly soluble in ether and alcohol, but readily so in chloroform and benzene. On heating, it sublimes in microscopic needles. It contains no hydroxyl group, being unaffected by prolonged boiling with acetic anhydride, and is not changed by boiling alcoholic potassium hydroxide. A determination of its specific rotatory power gave the following result:

0.2185, made up to 20 c.c. with chloroform, gave  $\alpha_D + 2.38'$  in a 1 dm. tube, whence  $[\alpha]_D + 120.5^\circ$ .

*Elateronemonophenylhydrazone*.—Elaterone and phenylhydrazine readily interact in acetic acid solution, but if the mixture be heated, only resinous products result. When, however, the reaction is carried out in the cold, and only allowed to proceed for about fifteen minutes, a *monophenylhydrazone* is formed. This crystallises from dilute acetic acid in golden-yellow plates, melting and decomposing at  $278^\circ$ :

0.0988 gave 5.8 c.c. N at  $24^{\circ}$  and 746 mm.  $N = 6.4$ .

$C_{30}H_{36}O_4N_2$  requires  $N = 5.7$  per cent.

*Elateronedioxime*.—Elaterone was boiled for some hours with an alcoholic solution of hydroxylamine. On concentrating the mixture, a dioxime separated in small, colourless plates, melting and decomposing at  $295^{\circ}$ .

0.2086 gave 11.0 c.c. N at  $18^{\circ}$  and 764 mm.  $N = 6.2$ .

$C_{24}H_{32}O_6N_2$  requires  $N = 6.5$  per cent.

It is therefore evident that elaterone contains two carbonyl groups, both of which appear to be ketonic, as on boiling it with chromic acid solution, it is much more slowly oxidised than would be the case with an aldehyde.

A quantity (1.5 grams) of elaterone was boiled for one hour with chromic acid (1.5 grams: 6 atoms of oxygen) in acetic acid solution. At the end of this time, however, 0.5 gram of elaterone was recovered unchanged. No definite oxidation products of elaterone have as yet been obtained.

## (2) Formation of a Compound, $C_{24}H_{32}O_4$ .

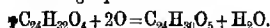
If "elateric acid" be subjected to a somewhat milder oxidation than that described in connexion with the formation of elaterone, two crystalline products are formed, in about equal amounts.

A quantity (2.5 grams) of "elateric acid" was dissolved in glacial acetic acid (25 grams), and to the solution chromic acid (1.6 grams) dissolved in water (3 grams) was added. The solution was heated on a water-bath for one hour, and then worked up as in the previously described oxidation. In this case, however, a crystalline product was obtained, melting at  $225-235^{\circ}$ , which, after fractional crystallisation from alcohol, was separated into two substances, one of which melted at  $295-300^{\circ}$ , and was evidently elaterone, while the other formed glistening plates, melting at  $230^{\circ}$ . The quantity of the second substance was only 0.2 gram. Like elaterone, it was neutral towards alkalis, and did not react with acetic anhydride, but the quantity of material available was too small for full investigation;

0.1175 gave 0.3224  $CO_2$  and 0.0895  $H_2O$ .  $C = 74.8$ ;  $H = 8.5$ .

$C_{24}H_{32}O_4$  requires  $C = 75.0$ ;  $H = 8.3$  per cent.

It thus appears probable that this substance is an intermediate compound in the formation of elaterone, and that it yields the latter according to the following equation:



With the object of continuing this investigation, an attempt was made to obtain a further quantity of  $\alpha$ -elaterin from a good specimen

of commercial colocynth pulp, but only a very small quantity of the desired compound could be isolated. This result is somewhat remarkable, as Power and Moore (*loc. cit.*) had previously obtained over 1 per cent. of  $\alpha$ -elaterin from Turkish colocynth pulp. It is therefore evident that the amount of  $\alpha$ -elaterin contained in colocynth pulp may vary very greatly.

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#### CXCIV.—*The Molecular Complexity of Amides in Various Solvents. Part III. Amides in Aqueous Solution.*

By ANDREW NORMAN MELDRUM (Carnegie Research Fellow) and  
WILLIAM ERNEST STEPHEN TURNER.

In order to bring the phenomenon of electrolytic dissociation in aqueous solution into connexion with fundamental ideas of electricity, J. J. Thomson advanced the hypothesis that water produces dissociation by reason of its high dielectric constant: "If the forces which hold the molecule together are electrical in their origin . . . these forces will be very much diminished when the molecule . . . is surrounded by a substance like water possessing a very large specific inductive capacity" (*Phil. Mag.*, 1893, [v], 36, 313).

It is this hypothesis of Thomson which has originated the study of solvents in connexion with their dielectric constants, particularly of such as have a large constant. Notably, hydrocyanic acid, which has the constant 95, has been studied by Schlundt (*J. Physical Chem.*, 1901, 5, 157); and formamide (constant  $>84$ ) by Walden (*Zeitsch. physikal. Chem.*, 1905, 54, 179, 181). The dielectric constant of water is 80.

Originally applied to the electrolytic dissociation of salts, Thomson's hypothesis was brought to bear by Nernst on the phenomenon of association in solution (*Zeitsch. physikal. Chem.*, 1894, 13, 535). Association of a solute, on the supposition that this is caused by forces electrical in their origin, should be allowed by a solvent of low dielectric constant, and prevented by a solution of which the constant is high. This corollary of Thomson's proposition is denoted in this paper by the term the "Nernst-Thomson rule."

The authors have subjected the Nernst-Thomson rule to a very careful examination. They have already found good agreement



with the rule for solutions of the amides—known to have a tendency to association—in five organic solvents, namely, ethyl alcohol, acetone, chloroform, ether, and benzene (Trans., 1908, 93, 876; this vol., 1605). *n*-Butyramide, for instance, is highly associated in benzene, of which the dielectric constant is 2.3 at 18°, and normal in ethyl alcohol, of which the constant is 25.4 at 18.5°.

Water, however, presented notable exceptions to the rule. Certain amides, in solution in water, namely, benzamide, salicylamide, acetanilide, and dichloroacetamide, gave quite high molecular weights. These results were against all precedent and theory. No one had previously drawn attention to the fact that substances may be associated to as great an extent in water as in benzene. Further, the rule that the authors set out to test was found to hold good for five organic solvents, and ought to have proved specially sound in the case of water. Yet in this very case it broke down. The authors, in deciding to study the matter further, did so because the phenomenon of association in aqueous solution seemed to them of considerable importance in various directions.

#### EXPERIMENTAL.

The amides were the same as those used in part II of this series. The molecular weights were determined by the ebullioscopic method, using the same apparatus as before. The amount of solvent was ascertained both by weight and volume, and the authors have considered it advisable to give both sets of data. The reason for this is that the concentration necessary to produce a certain elevation of the boiling point of water is considerable, three to six times that for other solvents, and in consequence the divergence between weight and volume results is marked.

The solvent constants for water are (volume) 530, (weight) 510. In the following tables,\*

$V$  denotes volume of solution in c.c.

$W$  denotes weight of solvent in grams.

$\Delta$  denotes elevation of boiling point (corrected).

$N_v$  denotes the number of milligram-molecules of solute per 100 grams of solvent.

M.W. denotes molecular weight determined by the volume method.

M.W. " " " " " " weight " "

\* These symbols were used in Part II., but the meaning of  $N_v$  was incorrectly stated there (*loc. cit.*, p. 1608).

## COMPLEXITY OF AMIDES IN VARIOUS SOLVENTS. PART III. 1807

## Solvent—Water.

$\eta$ .	$W$ .	$\Delta$ .	$N$ .	M.W.	M.W.
<i>Propionamide</i> (M.W. 73.1), 2.083 grams.					
20.6	17.88	0.705	159.8	75.9	84.5
24.6	21.26	0.596	134.0	75.4	83.8
28.8	25.18	0.507	113.2	75.5	83.2
36.7	33.50	0.382	85.1	78.7	83.0
42.0	37.98	0.336	75.2	78.1	83.3
<i>Methylacetanilide</i> * (M.W. 149), 2.681 grams.					
22.5	18.13	0.162	99.2	389	465
25.3	21.33	0.137	84.3	395	468
3.069 grams.					
22.1	17.70	0.141	116.3	523	627
2.037 grams.					
22.5	25.8	0.093	53.0	393	434
<i>n-Butyramide</i> (M.W. 87.1), 1.975 grams.					
31.2	27.52	0.346	81.5	97.0	104.6
37.8	34.07	0.289	66.6	95.7	102.3
43.1	39.32	0.261	57.7	93.0	98.1
49.7	47.67	0.227	49.8	92.8	97.4
<i>iso-Butyramide</i> (M.W. 87.1), 2.060 grams.					
31.0	27.82	0.363	85.8	97.0	104.8
34.6	31.14	0.319	75.9	99.0	105.8
42.3	38.24	0.262	61.8	98.5	104.9
50.1	45.89	0.223	51.5	97.6	102.7
<i>Valeramide</i> (M.W. 101.1), 1.920 grams.					
24.3	20.86	0.345	91.0	122	136
28.8	25.24	0.296	75.2	119	131
35.1	31.74	0.248	59.8	117	124
42.1	38.14	0.209	49.8	115	123
<i>iso-Butylacetamide</i> (M.W. 115.1), 2.209 grams.					
32.1	26.38	0.224	67.6	163	177
37.8	33.73	0.202	56.9	153	165
1.699 grams.					
25.2	22.36	0.218	66.0	164	178
30.6	27.17	0.183	54.3	161	174
<i>Glycollamide</i> (M.W. 75), 1.603 grams.					
26.0	23.94	0.447	89.3	73.2	76.4
30.3	28.13	0.395	76.0	70.9	73.6
36.4	34.13	0.300	62.6	77.7	79.8
45.7	42.94	0.236	49.8	78.7	80.7

\* This substance is volatile with steam, a source of error which we reduced to a minimum by carrying out several experiments, each giving one molecular-weight result. In addition, four molecular-weight determinations were made in series, with the object of observing the extent of distillation during the course of the work. The amount of anilide originally taken was 2.68 grams, and the amount remaining, after the 35 minutes which the series occupied, was found to be 1.94 grams.

*Solvent—Water.*

<i>T.</i>	<i>W.</i>	$\Delta$	<i>N.</i>	<i>M.W.</i>	<i>M.W.</i>
<i>Lactamide</i> (M.W. 89.1), 2.601 grams.					
22.8	19.39	0.717	147.5	84.3	95.4
26.4	22.92	0.612	124.7	85.2	94.6
30.9	27.44	0.517	105.2	86.3	94.1
36.7	32.94	0.431	86.8	87.1	93.4
<i>Phenylacetamide</i> (M.W. 135), 2.612 grams.					
25.0	21.69	0.297	89.2	186	207
29.2	25.40	0.269	76.2	176	196
41.1	37.07	0.210	53.4	180	171
2.101 grams.					
27.8	22.90	0.244	68.0	164	192
31.0	27.30	0.222	57.0	161	177
34.7	31.72	0.204	49.1	157	166
42.9	39.32	0.175	39.6	148	156
<i>Formanilide</i> (M.W. 121), 2.137 grams.					
26.6	23.65	0.238	74.6	179	194
32.0	29.00	0.211	60.8	168	173
1.548 grams.					
26.7	24.24	0.188	52.7	163	173
30.9	27.91	0.171	45.8	155	165
36.8	33.91	0.145	37.7	154	161
<i>Glycollanilide</i> (M.W. 151), 2.215 grams.					
30.5	27.34	0.210	53.6	183	197
36.3	33.24	0.177	44.1	183	192
42.9	39.14	0.159	37.4	172	181
52.3	48.26	0.134	30.4	167	176
<i>Lactanilide</i> (M.W. 165), 2.313 grams.					
23.7	20.95	0.230	66.9	224	245
27.5	24.05	0.213	58.2	209	230
31.2	27.59	0.188	50.8	209	227
35.1	31.57	0.171	44.4	204	218
42.0	38.02	0.149	36.8	196	208
<i>Phenylcarbamide</i> (M.W. 136), 1.174 grams.					
23.2	21.84	0.172	39.5	156	159
27.6	25.19	0.153	34.3	148	155
30.5	28.34	0.141	30.4	145	150
44.6	41.59	0.102	20.7	137	141

*Experiment at the Freezing Point.**Urethane* (M.W. 89.1).

<i>W.</i>	<i>w</i> (grams).	$\Delta$	<i>M.W.</i>
19.09	0.398	0.438	88.4
19.09	0.815	0.874	90.3
19.09	1.019	1.084	91.0

*Examination of Results.*

The results of the present investigation suggest that in water, despite its high dielectric constant, association is quite a frequent occurrence. To the four amides already found to be associated in water, the authors are able to add eleven out of the fourteen amides recently tested. (In what follows, the results of the previous investigation are shown by an asterisk.) Acetamide,\* monochloroacetamide,\* carhamide,\* malonamide,\* glycollamide, lactamide, and urethane are unassociated. Trichlorolactamide\* is doubtful. Propionamide, *n*-butyramide, *isobutyramide*, valeramide, *isobutylacetamide*, glycollanilide, lactanilide, formanilide, acetanilide,\* methylacetanilide, phenylacetamide, phenylcarbamide, benzamide,\* salicylamide,\* and dichloroacetamide\* are associated.

This association presents a remarkable feature, which is best shown by putting the extent of association in water and in benzene side by side. As a means of comparison, the molecular weights and association factors are calculated at a concentration of 50 milligram-molecules per 100 c.c. of solvent, obtained from the weight data which, for solutions in benzene, were not given in full in the tables:

	In water.		In benzene.	
	M.W.	A. F.	M.W.	A. F.
Propionamide.....	83.0	1.14	148	2.03
<i>n</i> -Butyramide.....	97.6	1.12	172	1.98
<i>isobutyramide</i> .....	102.8	1.18	169	1.94
Valeramide.....	123.0	1.22	184	1.82
<i>isobutylacetamide</i> .....	173.0	1.50	206	1.79
Urethane.....	—	—	142	1.6
Glycollamide.....	80.5	1.07	—	—
Lactamide.....	92.0	1.03	—	—
Glycollanilide.....	196.0	1.30	340.	2.25
Lactanilide.....	227.0	1.38	320	1.94
Formanilide.....	170.0	1.42	180	1.49
Acetanilide.....	194.0	1.44	—	—
Methylacetanilide.....	350.0	3.00	155	1.04
Phenylacetamide.....	170.0	1.26	—	—
Phenylcarbamide.....	170.0	1.25	—	—

A striking regularity is displayed in these data, namely, that the greater the tendency of a substance to molecular association in benzene, the less is its tendency in aqueous solution. As the figures in our first paper show, salicylamide is less associated in benzene than benzamide is, and in water the positions are reversed. Again, with the exception only of a slight deviation in the case of propionamide and *n*-butyramide in water, due possibly to slight experimental error, the tendency to molecular association in water rises from propionamide to *isobutylacetamide*, and falls in this order in benzene. Methylacetanilide, which has the normal molecular weight in benzene, shows apparent association of a very high order

in water. Lactamide is not associated in water, and according to our rule should be strongly associated in benzene. Unfortunately, it is not soluble enough in benzene for the purpose, but there is good reason to think it is associated. One of us, in conjunction with Mr. E. W. Merry, has ascertained that it is strongly associated in the fused state. Phenylacetamide is moderately associated in water, in chloroform, and in the fused state. Urethane, which is associated in benzene, seemed to be associated in water also. It was suspected that the substance decomposes in water at  $100^{\circ}$ , and therefore the ebullioscopic was discarded in favour of the cryoscopic method. There was then no sign of association.

*The Importance of the Phenomenon of Association in Water.*

The authors hold that the unexpected association in aqueous solution, which they have demonstrated in the case of the amides, is not limited to these substances, but is of frequent occurrence. They have studied the amides, in the first place, as being, usually, soluble enough at  $100^{\circ}$ , and at the same time non-volatile. But certain other observations of association have been made. Jones and Getman, by the cryoscopic method, showed that acetic, oxalic, and succinic acids tend to form associated molecules in water (*Amer. Chem. J.*, 1904, 32, 329).

The authors believe that this possibility of association in aqueous solutions has been left out of account in recent investigations to an injurious extent. Viscosity determinations as a means of detecting the formation of compounds between solute and solvent are in favour just now. From the determination of the viscosities of solutions in water of several organic acids, Tsakalotos (*Compt. rend.*, 1908, 146, 1146) was led to think that formic acid produces no hydrate, whilst acetic, propionic, and *n*-butyric acids yield hydrates of the type  $R \cdot CO_2H, H_2O$ . Previously, however, Jones and Getman had concluded that there is no appreciable tendency on the part of acetic, oxalic, succinic, tartaric, and citric acids to form hydrates (*loc. cit.*, p. 338). Acetic acid certainly, and propionic and butyric probably, associate in water. Hence the authors would urge the necessity of considering that the molecules of the solute may associate with one another, as well as combine with water. A method of interpreting viscosity data which shall distinguish between these two possibilities is urgently needed.

In connexion with the "hydrate theory," the authors have made certain experiments of a similar character to those of Caldwell (*Proc. Roy. Soc.*, 1906, A, 78, 272) and of H. E. Armstrong (*ibid.*, 1907, A, 79, 576). These experiments consisted in observing the effect of several salts on the rate of inversion of sucrose by acids,

and on the rate of hydrolysis of methyl acetate by hydrochloric acid. In place of a salt, that is, a dissociated substance, the authors have used methylacetanilide, which, as they had found, is strongly associated in water.

*Experiments on the Inversion of Sucrose.*

The effect of sodium chloride and of methylacetanilide on the inversion of sucrose was measured. Weight-normal solutions were used throughout. The temperature of experiment in each case was 40°.

*Experiment 1.*—One hundred c.c. of *N*/4-hydrochloric acid were mixed with 100 c.c. of 20 per cent. sucrose solution. Mean value of seven measurements of velocity constant,  $K = 7.42 \times 10^{-3}$ . Extremes,  $7.15$  and  $7.70 \times 10^{-3}$ .

*Experiment 2.*—Solutions as before, with addition of 5 grams (0.085 mol.) of sodium chloride. Mean (5 measurements),  $K = 8.65 \times 10^{-3}$ . Extremes,  $8.60$  and  $8.71 \times 10^{-3}$ .

*Experiment 3.*—Solutions as before, with addition of 5 grams (0.033 mol.) of methyl acetanilide. Mean (8 measurements),  $K = 8.65 \times 10^{-3}$ . Extremes,  $8.49$  and  $8.78 \times 10^{-3}$ .

Equal amounts by weight of sodium chloride and methylacetanilide had apparently the same effect in accelerating the inversion of sucrose.

*Experiments on the Hydrolysis of Ethyl Acetate.*

Weight-normal solutions were again used. The temperature was 25°, which allowed only of a low concentration of methylacetanilide.

*Experiment 1.*—Two c.c. of ethyl acetate were mixed with 100 c.c. of *N*/2-hydrochloric acid. Mean of five measurements,  $K = 2.63 \times 10^{-3}$ . Extremes,  $2.52$  and  $2.71 \times 10^{-3}$ .

*Experiment 2.*—Solution as before, with addition of 4 grams (0.068 mol.) of sodium chloride. Mean (6 measurements),  $K = 3.24 \times 10^{-3}$ . Extremes,  $3.14$  and  $3.31 \times 10^{-3}$ .

*Experiment 3.*—Solution as before, with addition of 2 grams (0.026 mol.) of methylacetanilide. Mean (6 measurements),  $K = 3.05 \times 10^{-3}$ . Extremes,  $3.01$  and  $3.08 \times 10^{-3}$ .

The results show that the presence of methylacetanilide has an effect on these two chemical changes of the same kind as that due to sodium chloride. In the case of both hydrolysis and inversion the change is accelerated. Of the two substances, methylacetanilide has the greater effect, molecule for molecule. Supposing the withdrawal of water of hydration, by the added substance, to be the explanation of the accelerated inversion, or hydrolysis, as the case may be, it

is obvious that methylacetanilide must be much more hydrated in solution than sodium chloride; for the same effect on the inversion of sucrose is produced by equal weights of the two substances, that is, by 1 molecule of methylacetanilide for 2.5 molecules of sodium chloride. If we assume that at the particular concentration employed, namely, 2½ per cent., the molecular hydration of sodium chloride is 14 (see, for example, Philip, *Trans.*, 1907, 91, 711), that of methylacetanilide must be about 35. Interpretation in this manner of the influence of methylacetanilide seems quite impossible. One cannot admit the possibility of combination between water and methylacetanilide to such an extent in the total absence of other evidence in this direction. There is, indeed, evidence to the contrary. Supposing methylacetanilide to combine with 35 molecules of water, we should expect it to give an abnormally high elevation of boiling point; for water is withdrawn from the rôle of solvent, and the solution is thereby concentrated. The reverse is the case: we find instead an abnormally low elevation. The hydrate theory, here at any rate, is entirely inapplicable.

At the present time, much work is being done on the problem of solution by the employment of what is regarded as an "indifferent" substance; that is, the substance and the solvent are supposed to be indifferent to one another. The method is to observe either the effect on the solubility of the indifferent substance, produced by the presence of another substance, or vice versa, the effect on the solubility of the other substance due to the presence of the indifferent substance (compare Usher, *Trans.*, 1910, 97, 66; Fox and Gauge, *loc. cit.*, 377; and Findlay and Creighton, *loc. cit.*, 559). It may be pointed out here that of the substances employed in these researches, quite a number, either in the liquid state or in suitable solvents, are known to be associated.

That substances which, for the purposes of investigation, were regarded as "indifferent," should have a tendency to association, is a state of things which was probably not intended. Hence it is possible that Usher's test of Jahn's hypothesis, namely, that the solubility of a gas in a dilute solution of a non-volatile, indifferent substance is the same, under the same conditions of temperature and pressure, as in the pure solvent, may not be valid (Usher, *loc. cit.*, 76). In the opinion of the authors, associated substances cannot be regarded as indifferent, and this opinion receives strong support from the experiments just detailed, in which methylacetanilide was employed. In these experiments, methylacetanilide, which is known to be associated, and sodium chloride, which is not supposed to be "indifferent," were found to produce effects of the same kind.

One line along which the working out of the problem suggests itself, by reason of the fact that the more nearly normal in organic solvents is the amide, the more strongly it appears to be associated in water, is that the molecular structure of water must be taken into account, in such a way as to admit that sometimes the structure may become more complex and sometimes simpler.

Here the authors would draw attention to the work of P. W. Robertson, on solution in phenol (*Trans.*, 1903, **83**, 1904; 1904, **85**, 1425, 1617; 1905, **87**, 1574; 1906, **89**, 567), as having led him to results and conclusions in some respects similar to their own. He found that in phenol, itself an associated substance, the hydrocarbons and their halogen derivatives have high molecular weights. This abnormality the author believed "to be connected with the association of the phenol molecules, as the substituted phenols, which are less associated, tend [when used as solvents] to give normal results" (*Trans.*, 1906, **89**, 570).

Within the last three years, H. E. Armstrong (*Proc. Roy. Soc.*, 1908, **81**, A, 80; 1909, **81**, B, 94) has formulated a theory of aqueous solution which involves the assumption that molecules of different degrees of complexity are present in liquid water, the various processes of solution involving the operation of these differently sized molecules.

The authors find themselves in agreement with the theory in so far as it appears to them necessary to take account of probable changes in the molecular complexity of water when solution occurs, differing with the nature of the solute. Moreover, since a substance which possesses a high molecular complexity has usually a high dielectric constant, these changes may well be accompanied by alterations in the dielectric constant of water, which cannot but react on the condition of the solute.

The authors desire to thank Mr. E. W. Merry, M.Sc., of the University of Sheffield, for carrying out the experiments on the inversion of sucrose and the hydrolysis of ethyl acetate.

The materials employed in this investigation were obtained by means of grants from the Government Grant Committee of the Royal Society and the Executive Committee of the Carnegie Trust for the Universities of Scotland.

THE UNIVERSITY,  
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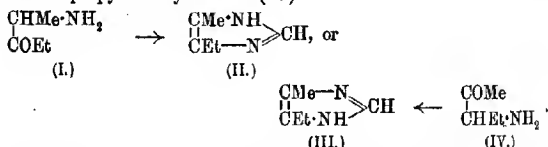


CXCv.—*The Tautomerism of Glyoxalines and the Constitution of Pilocarpine.*

By FRANK LEE PYMAN.

SINCE the suggestion of Pinner and Schwarz (*Ber.*, 1902, 35, 2441), followed by the experimental proof adduced by Jowett (*Trans.*, 1903, 83, 438), that the glyoxaline radicle is contained in the alkaloid pilocarpine, and later the discovery by Pauly (*Zeitach. physiol. Chem.*, 1904, 42, 508) of this radicle in histidine, synthetic experiments with glyoxalines have attracted the attention of a number of chemists. Quite recently an added stimulus has been given to the work through the discovery by Barger and Dale (*Proc.*, 1910, 26, 128) that  $\beta$ -iminazolyethylamine, a compound which was recently synthesised by Windaus and Vogt (*Ber.*, 1907, 40, 3691), is one of the active principles of ergot.

Some years ago Dr. Jowett (Jowett and Potter, *Trans.*, 1903, 83, 464; Jowett, *Trans.*, 1905, 87, 405), with a view to syntheses in this field, commenced a series of investigations, which will be referred to in detail later, and more recently, being unable to resume the work personally, requested the present author to continue it. The most important result of the present investigation is the proof that glyoxalines, containing a free imino-hydrogen atom, are tautomeric, a fact which previous research on the subject had already made probable. Thus, Jänecke (*Ber.*, 1899, 32, 1098) prepared, by the oxidation of the mercaptan formed by the action of potassium thiocyanate on  $\alpha$ -aminodiethyl ketone (I), the same methylethylglyoxaline (II or III) which Gabriel and Posner (*Ber.*, 1894, 27, 1037) had previously obtained in a similar manner from  $\alpha$ -aminopropyl methyl ketone (IV):

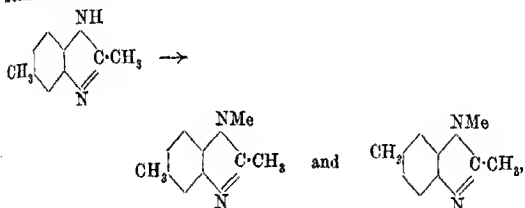


This method of synthesis does not enable any conclusion to be drawn as to which of the two isomerides, 5-methyl-4-ethylglyoxaline (II) and 4-methyl-5-ethylglyoxaline (III), is to be expected in each case, but it was inferred that a different one of the two would be expected in the two cases; the fact that the same methylethylglyoxaline was actually obtained in each case consequently showed either that this compound is tautomeric, or that one of the two forms (II) and (III) is the more stable. Jänecke thought the former

view the more probable, and suggested that the imino-hydrogen atom vibrated between the nitrogen atoms in the same way as it does, according to Knorr (*Annalen*, 1894, **279**, 188), in the case of the pyrazoles;



Several years later, Otto Fischer (*J. pr. Chem.*, 1906, [ii], **73**, 419; 1907, [ii], **75**, 88) prepared the 1:2:5- and 1:2:6-trimethylbenzimidazoles by the action of methyl iodide on 2:5-dimethylbenzimidazole:



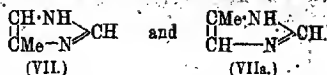
and thus showed that this compound is tautomeric.

In consequence of this result, and in order to demonstrate that the simple glyoxalines are also probably tautomeric, Gabriel (*Ber.*, 1908, **41**, 1926), who appears to have overlooked Jänecke's paper, brought forward another example of the formation from two different amino-ketones of a single 4:5-disubstituted glyoxaline, namely, phenylmethylglyoxaline. On the other hand, neither Jowett and Potter (*loc. cit.*) in the methylation of 4(or 5)-methylglyoxaline, nor Pinner (*Ber.*, 1905, **38**, 1535) in the ethylation of 4(or 5)-phenylglyoxaline, isolated two isomeric *N*-alkyl derivatives, and further, in more recent publications, both Pauly and Gundermann (*Ber.*, 1908, **41**, 4005) and Windaus (*Ber.*, 1909, **42**, 762) describe experiments with "*α*-*N*-dimethyliminazol"—presumably the methylation product of *α*-methylglyoxaline, that is, 4(or 5)-methylglyoxaline. The tautomerism of glyoxalines has therefore not hitherto been generally recognised.

A definite proof of the tautomerism of simple glyoxalines is now brought forward, for it has been found that 4(or 5)-methylglyoxaline yields, on methylation, a mixture of two isomeric *N*-methyl derivatives, 1:4- and 1:5-dimethylglyoxaline (V and VI) respectively:



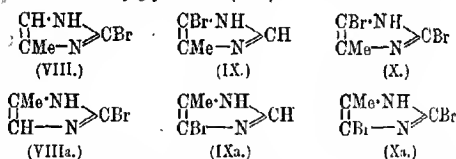
and therefore reacts according to both the formula (VII and VIIa).



It may therefore be considered to react as a compound in which the hydrogen atom of the imino-group alternates in position between the two nitrogen atoms as suggested by Jänecke (*loc. cit.*) in the case of methylethylglyoxaline.

The formation of two isomeric *N*-methyl derivatives by the methylation of a glyoxaline has been confirmed by the methylation of the bromo-derivatives of 4(or 5)-methylglyoxaline.

The action on 4(or 5)-methylglyoxaline of bromine in a quantity sufficient to form a monobromo-substitution product has been tried at different temperatures, and it has been found that, even at  $-10^{\circ}$ , the monobromo-derivative is accompanied by a considerable proportion of the dibromo-derivative, a corresponding quantity of 4(or 5)-methylglyoxaline being consequently unattacked. Only one monobromo-derivative has been isolated, and there is at present no evidence to show whether the substituent bromine atom occupies the 2- or the 4(or 5)-position. This compound is tautomeric, and reacts either as 2-bromo-4-methylglyoxaline (VIII) and 2-bromo-5-methylglyoxaline (VIIIa) or as 5-bromo-4-methylglyoxaline (IX) and 4-bromo-5-methylglyoxaline (IXa):



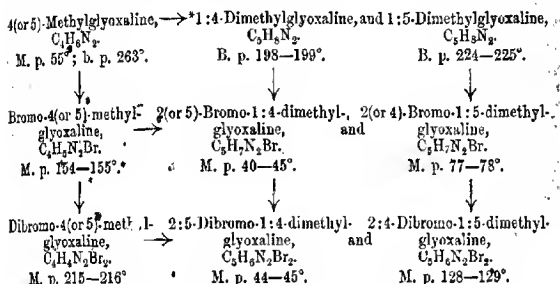
The dibromo-derivative is also tautomeric, and reacts as 2:5-dibromo-4-methylglyoxaline (X) and 2:4-dibromo-5-methylglyoxaline (Xa).

Bromo-4(or 5)-methylglyoxaline yields, on methylation, a mixture of two isomeric bromodimethylglyoxalines, which melt at  $40-45^{\circ}$  and  $77-78^{\circ}$  respectively.

Dibromo-4(or 5)-methylglyoxaline similarly yields, on methylation, a mixture of two isomeric dibromodimethylglyoxalines, melting at  $44-45^{\circ}$  and  $128-129^{\circ}$ . The two dimethylglyoxalines obtained by the methylation of 4(or 5)-methylglyoxaline distil at  $198-199^{\circ}$  and  $224-225^{\circ}$ , and in order to determine which of the isomeric bromo- and dibromo-dimethylglyoxalines was derived from each dimethylglyoxaline, the latter bases were also brominated. Although the bromination of the two isomerides was carried out under pre-

cisely similar conditions, the results showed an interesting difference, the dimethylglyoxaline boiling at 198—199° yielding chiefly the corresponding monobromo-derivative which melts at 40—45°, and very little of the dibromodimethylglyoxaline which melts at 44—45°; whilst the dimethylglyoxaline boiling at 224—225° gave very little of the corresponding monobromodimethylglyoxaline melting at 77—78°, but chiefly the dibromodimethylglyoxaline melting at 128—129°.

The mutual relations between the isomeric dimethylglyoxalines and the various bromo-derivatives are shown by the following scheme:



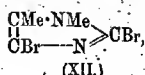
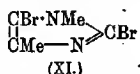
\* The numbers are inserted in anticipation of the conclusions drawn later.

The question as to which series has the 1:4 and which the 1:5 arrangement of methyl groups is difficult to determine, and no direct evidence bearing on this point is brought forward at present. Fortunately, however, this matter can be settled with a high degree of probability by consideration of the relative affinities of the two dibromodimethylglyoxalines. These compounds are weak bases, and it has been found that the isomeride melting at 128—129° is very much more readily extracted by means of chloroform from its solution in 10 per cent. hydrochloric acid than the isomeride melting at 44—45°; the latter is therefore the stronger base.

Now, of the two nitrogen atoms in the glyoxaline molecule, the iminic nitrogen atom occupies a similar position to the nitrogen atom of pyrrole, and is almost devoid of basic properties. Glyoxalines behave as mono-acid bases, and the fact that their basicity is due to the nitrogen atom 'N' has been clearly shown by Pinner and Schwarz (*loc. cit.*) by the formation of a mixture of mono-alkylamines by the degradation of alkyl salts of *N*-substituted glyoxalines.

Consideration of the formulae of the two isomeric dibromodi-

methylglyoxalines (XI and XII) shows that the basic 3-nitrogen atom:



is in both cases in close proximity to the strongly negative substituent bromine atom in the 2-position; the position of the other bromine atom relative to the 3-nitrogen atom is different in the two cases, and it seems reasonable to suppose that 2:5-dibromo-1:4-dimethylglyoxaline (XI), in which the second bromine atom is at a distance from the 3-nitrogen atom, will be a stronger base than 2:4-dibromo-1:5-dimethylglyoxaline (XII), in which these groups are close together. On the assumption that this view is correct, the compound melting at 44—45° is 2:5-dibromo-1:4-dimethylglyoxaline, and consequently the dimethylglyoxaline boiling at 198—199° is 1:4-dimethylglyoxaline, the compound melting at 128—129° is 2:4-dibromo-1:5-dimethylglyoxaline, and the dimethylglyoxaline boiling at 224—225° is 1:5-dimethylglyoxaline.

The bearing of these results on the constitution of isopilocarpine has now to be discussed.

By the distillation of this alkaloid with soda-lime, Jowett (Trans., 1903, 83, 438) obtained a number of glyoxaline derivatives, of which one was shown to be a dimethylglyoxaline. For the purpose of comparison, Jowett and Potter (Trans., 1903, 83, 464) prepared by the methylation of 4(or 5)-methylglyoxaline an *N*-methyl derivative, which they regarded as a simple substance, either 1:4- or 1:5-dimethylglyoxaline. The aurichloride and platinichloride of this base, after suitable crystallisation, were shown to be identical with the aurichloride and platinichloride respectively of the dimethylglyoxaline obtained from isopilocarpine; the picrate of the synthetic base, however, although having the same melting point—167°—as the picrate of the dimethylglyoxaline from isopilocarpine, was not identical with the latter, since the mixture melted at 140—145°. These facts led Jowett to the conclusion that the dimethylglyoxalines derived from isopilocarpine, and obtained by the methylation of 4(or 5)-methylglyoxaline respectively, were isomeric and not identical, and he also concluded that they were the 1:4- and 1:5-dimethylglyoxalines, but that there was no evidence to show which of the two was 1:4 and which 1:5.

The repetition of the methylation of 4(or 5)-methylglyoxaline on a larger scale, which has been made possible by Windaus and Knoop's discovery (Ber., 1905, 38, 1166) of a convenient method for the preparation of this compound, has shown that the product obtained is a mixture of the 1:4- and 1:5-isomerides. A com-

parison of the properties of the two isomerides and their salts with those of the dimethylglyoxaline from *isopilocarpine* recorded by Jowett (*loc. cit.*) is tabulated below:

		1 : 4.	1 : 5.	From <i>isopilocarpine</i> .
Base.....	B. p. ....	198—199°	224—225°	210—215°
	Sp. gr. ....	0.997	1.021	—
	$n_D^{20}$ .....	1.49042	1.49963	—
Aurichloride .....	M. p. ....	137—138°	218—219°	214—215°
	Solubility in alcohol	easily	sparingly	—
Platinichloride ...	M. p. ....	233°	246°	238—239°*
	Solubility in water.	fairly easily	sparingly	—
Picrate .....	M. p. ....	167—168°	168—169°	167°
Hydrochloride ...	M. p. ....	168—169°	194—195°	—
Hydr. gen. oxalate.	M. p. ....	105—106°	133—134°	—

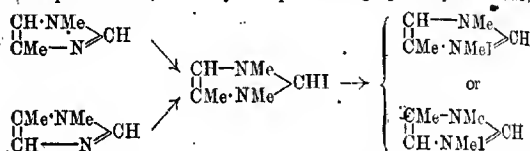
\* When heated fairly quickly, this salt melted at 247°.

Through the kindness of Dr. Jowett, the author has had the opportunity of examining specimens of the picrate and platinichloride of the dimethylglyoxaline obtained from *isopilocarpine*. The picrate melted at 167—168°, and mixtures of approximately equal amounts of this salt with (1) 1 : 4-dimethylglyoxaline picrate at 140—145° and (2) 1 : 5-dimethylglyoxaline picrate at 167—168°. The platinichloride, when slowly heated, decomposed at 238—239°, and mixtures with (1) 1 : 4-dimethylglyoxaline platinichloride at 220° and (2) 1 : 5-dimethylglyoxaline platinichloride at 239°; when fairly quickly heated, however, the platinichloride decomposed at 247°, and the mixture with 1 : 5-dimethylglyoxaline platinichloride at 248°; the platinichloride of the dimethylglyoxaline from *isopilocarpine* is sparingly soluble in water. Consideration of the table and the above facts shows that the dimethylglyoxaline from *isopilocarpine* is identical with the isomeride of higher boiling point, which there is good reason to believe is 1 : 5-dimethylglyoxaline.

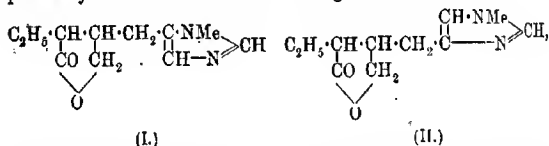
It is evident that Jowett and Potter's synthetic dimethylglyoxaline, which distilled mainly at 203° and had a specific gravity of 1.003, consisted chiefly of the 1 : 4-isomeride of lower boiling point; the picrates of the two isomerides being of a similar solubility in water; they eventually obtained, after crystallisation of their picrate, the pure picrate of 1 : 4-dimethylglyoxaline; recrystallisation of the aurichloride of their base from alcohol, however, gave them the pure 1 : 5-dimethylglyoxaline aurichloride, which is sparingly soluble in this solvent, whereas 1 : 4-dimethylglyoxaline aurichloride is easily soluble; similarly, recrystallisation of the platinichloride of their base from water yielded 1 : 5-dimethylglyoxaline platinichloride, which is sparingly soluble in water, the

1: 4-dimethylglyoxaline platinichloride remaining in the mother-liquors.

The methiodide prepared by Jowett and Potter from the synthetic dimethylglyoxaline may be obtained by the action of methyl iodide on either 1: 4- or 1: 5-dimethylglyoxaline. A similar case of the formation of only one methiodide from two isomeric benziminazoles has previously been described and explained by Otto Fischer (*loc. cit.*), on the assumption that methyl iodide is combined at the unsaturated linking, and that the compound produced then rearranges itself, forming the more stable of the two possible substituted ammonium iodides. This explanation is also applicable to the present case, and may be represented graphically as follows:



In conclusion, it may be pointed out that of the two alternative isomeric formulæ (I) and (II) put forward by Jowett (*loc. cit.*) for isopilocarpine (compare also Pinner and Schwarz, *loc. cit.*), (I), which depicts the alkaloid as a 1: 5-substituted glyoxaline, is supported by the fresh evidence now brought forward:



and since Jowett has shown (Trans., 1905, **87**, 794) that isopilocarpine and pilocarpine are stereoisomerides, this evidence is equally applicable to the latter alkaloid.

#### EXPERIMENTAL.

##### *Methylation of 4(or 5)-Methylglyoxaline: Separation of the Isomeric 1: 4- and 1: 5-Dimethylglyoxalines.*

One hundred grams of 4(or 5)-methylglyoxaline were well shaken with 360 c.c. of 20 per cent. aqueous sodium hydroxide and 25 grams of methyl sulphate, the mixture being kept cold by running water; five further quantities of 120 c.c. of 20 per cent. aqueous sodium hydroxide and 25 grams of methyl sulphate were added successively with thorough shaking during the course of an hour. The liquor was then completely extracted with chloroform, and the extract

dried with anhydrous potassium carbonate. After removal of the solvent, the resulting oil was distilled once under diminished pressure, and then fractionated three times under normal pressure, fractions being collected every 10° between 190° and 250°. As a considerable proportion of the oil distilled above 250°, it appeared that a part of the 4(or 5)-methylglyoxaline had escaped methylation, and the fractions boiling above 230°, and amounting to 31 grams, were consequently re-methylated. The product was fractionated, and the fractions suitably combined with those from the first methylation.

At this stage the products were as follows:

B. p.	190—200°	200—205°	205—210°	210—215°	215—220°	220—230°
Grams	6.0	10.0	16.2	7.5	8.0	5.0

After twelve fractional distillations of the above under normal pressure, the following fractions were obtained:

B. p.	195—200°	200—202°	202—205°	205—210°	210—215°	215—220°
Grams	17.0	5.0	3.8	3.6	2.3	4.5
B. p.	.....	.....	220—225°	.....	above 225°	.....
Grams	.....	.....	8.4	.....	3.8	.....

The first fraction, b. p. 195—200°, distilled mainly at 198—199°, and represented nearly pure 1:4-dimethylglyoxaline. It was neutralised with dilute hydrochloric acid, and precipitated with picric acid, when 42 grams of the picrate, having the correct melting point, 167—168° (corr.), were obtained. After regeneration from the picrate, 1:4-dimethylglyoxaline distilled at 198—199° (corr.).

The fraction distilling at 220—225° was similarly converted into the picrate, and gave at first a quantity of pure 1:5-dimethylglyoxaline picrate, melting at 168—169° (corr.); the mother liquors and the picrates from adjacent fractions gave the same salt in a crude condition, and this was purified by crystallisation from water; altogether 19 grams of this salt were obtained in a pure state. After regeneration from the picrate, 1:5-dimethylglyoxaline distilled at 224—225° (corr.).



The base is a colourless, mobile, deliquescent liquid, having an odour somewhat similar to that of pyridine. It boils at 198—199° (corr.), and did not solidify after keeping for several hours in an ice-chest. It is miscible with water, alcohol, ether, and chloroform in all proportions, and a considerable amount of heat is developed when it is mixed with water or chloroform. It has a sp. gr. of 0.997 at 15.5°/15.5°, and a refractive index of 1.49042 at 20°.



1822 PYMAN: THE TAUTOMERISM OF GLYOXALINES AND

0.1495 gave 0.3419  $\text{CO}_2$  and 0.1121  $\text{H}_2\text{O}$ .  $\text{C}=62.4$ ;  $\text{H}=8.3$ .

0.0538 „ 13.7 c.c.  $\text{N}_2$  at 25° and 774 mm.  $\text{N}=29.0$ .

$\text{C}_5\text{H}_8\text{N}_2$  requires  $\text{C}=62.5$ ;  $\text{H}=8.4$ ;  $\text{N}=29.2$  per cent.

The *hydrochloride* was obtained by neutralising the base with absolute alcoholic hydrochloric acid, and evaporating the salt to dryness in a vacuum desiccator over sulphuric acid. It separated in long, colourless, very deliquescent needles, which melted at 168–169° (corr.):

0.1408 gave 0.1537  $\text{AgCl}$ .  $\text{Cl}=27.0$ .

$\text{C}_5\text{H}_8\text{N}_2\cdot\text{HCl}$  requires  $\text{Cl}=26.7$  per cent.

The *hydrogen oxalate* crystallises from absolute alcohol in prismatic needles, which, after drying in a vacuum, melt at 165–166° (corr.). This salt is readily soluble in water, but sparingly so in absolute alcohol:

0.1600, dried in a vacuum, gave 0.2637  $\text{CO}_2$  and 0.0841  $\text{H}_2\text{O}$ .

$\text{C}=44.9$ ;  $\text{H}=5.9$ .

$\text{C}_5\text{H}_8\text{N}_2\cdot\text{C}_2\text{H}_2\text{O}_4$  requires  $\text{C}=45.1$ ;  $\text{H}=5.4$  per cent.

The *aurichloride* crystallises from alcohol in yellow, transparent, pointed prisms, which melt at 137–138° (corr.). It is sparingly soluble in water, readily so in cold alcohol, and very readily so in hot alcohol:

0.1725 gave 0.0869  $\text{CO}_2$  and 0.0371  $\text{H}_2\text{O}$ .  $\text{C}=13.7$ ;  $\text{H}=2.4$ .

0.2224 „ 0.1010  $\text{Au}$ .  $\text{Au}=45.4$ .

$\text{C}_5\text{H}_8\text{N}_2\cdot\text{HAuCl}_4$  requires  $\text{C}=13.8$ ;  $\text{H}=2.1$ ;  $\text{Au}=45.2$  per cent.

The *platinichloride* crystallises from water in long, orange splinters, which decompose at 233° (corr.). It is fairly readily soluble in cold water, readily so in hot water, but almost insoluble in alcohol:

0.2015 gave 0.0647  $\text{Pt}$ .  $\text{Pt}=32.1$ .

$(\text{C}_5\text{H}_8\text{N}_2)_2\cdot\text{H}_2\text{PtCl}_6$  requires  $\text{Pt}=32.4$  per cent.

The picrate and methiodide have already been described by Jowett and Potter (*loc. cit.*), who obtained them from the synthetic dimethylglyoxaline.

The picrate crystallises from water in beautiful, long, flat, yellow needles, which melt at 167–168° (corr.). It is sparingly soluble in cold water, but readily so in hot water.

The methiodide is produced with considerable evolution of heat when equimolecular proportions of the base and methyl iodide are mixed. It crystallises from absolute alcohol in long, stout, colourless splinters, which, when dried at 100°, melt to a viscous liquid at 160–163° (corr.). When the salt is mixed with an equal amount of the methiodide of 1:5-dimethylglyoxaline, its melting point is unchanged.



The base is a colourless, mobile, deliquescent liquid, having an odour somewhat similar to that of pyridine, but less intense than that of the 1: 4-isomeride. It boils at 224–225° (corr.), and did not solidify after being kept for several hours in an ice-chest. It is miscible with water, alcohol, ether, and chloroform in all proportions, and a considerable amount of heat is developed when it is mixed with water or chloroform. It has a sp. gr. of 1.021 at 15.5°/15.5°, and a refractive index of 1.49963 at 20°:

0.1516 gave 0.3451 CO<sub>2</sub> and 0.1165 H<sub>2</sub>O. C=62.1; H=8.6.

0.0743 „ 18.8 c.c. N<sub>2</sub> at 24° and 770 mm. N=28.8.

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub> requires C=62.5; H=8.4; N=29.2 per cent.

The *hydrochloride*, prepared from the base and absolute alcoholic hydrochloric acid, separates in rectangular, oblong plates, melting at 194–195° (corr.); on evaporation of the solution in a vacuum over sulphuric acid. This salt is very deliquescent:

0.2134 gave 0.2313 AgCl. Cl=26.8.

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>.HCl requires Cl=26.7 per cent.

The *hydrogen oxalate* crystallised from absolute alcohol in stout, prismatic needles, which sintered at 132° and melted at 133–134° (corr.). This salt is readily soluble in water, but sparingly so in absolute alcohol:

0.1515 gave 0.2523 CO<sub>2</sub> and 0.0764 H<sub>2</sub>O. C=45.4; H=5.7.

C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>.C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires C=45.1; H=5.4 per cent.

The aurichloride, platinichloride, and picrate of, this base have previously been prepared by Jowett (Trans., 1903, **87**, 445) from the dimethylglyoxaline obtained by the distillation of isopilocarpine with soda-lime; the aurichloride and platinichloride were also prepared from synthetic dimethylglyoxaline (Jowett and Potter, *loc. cit.*), and identified with the corresponding salts obtained from the alkaloid. It is therefore only necessary to describe them shortly.

The aurichloride crystallised from alcohol in yellow needles, which sintered and deepened in colour at 165° and decomposed at 218–219° (corr.). This salt is sparingly soluble in water or alcohol.

The platinichloride separated on adding platinic chloride to the aqueous solution of the hydrochloride in orange, rectangular leaflets, which began to darken at 239° and decomposed at 246° (corr.). When heated more rapidly, this salt decomposes at 249° (corr.). This salt is sparingly soluble in cold water, and almost insoluble in alcohol.

The picrate crystallised from water in short, yellow needles, which melted at  $168-169^{\circ}$  (corr.). It is sparingly soluble in cold water, but readily so in hot.

A mixture of approximately equal parts of this salt and of 1:4-dimethylglyoxaline picrate gradually sintered, softened considerably at  $135^{\circ}$ , and melted to a clear liquid at  $140-145^{\circ}$ .

The methiodide is formed with considerable evolution of heat when equimolecular proportions of 1:5-dimethylglyoxaline and methyl iodide are mixed, and, after crystallisation from absolute alcohol, forms long, stout, colourless splinters, which, when dried at  $100^{\circ}$ , melt at  $160-163^{\circ}$  (corr.); this salt is identical with 1:4-dimethylglyoxaline methiodide (p. 1822).

#### *Bromination of 4(or 5)-Methylglyoxaline.*

To a solution of 100 grams of 4(or 5)-methylglyoxaline in 600 c.c. of chloroform, 200 grams of bromine diluted to 300 c.c. with chloroform were added drop by drop with mechanical stirring, the temperature being maintained at  $-10^{\circ}$  to  $-12^{\circ}$ . The addition of the bromine occupied an hour, and the liquor was stirred for another half hour. It then formed a clear, pale brown solution, but when removed from the freezing mixture became turbid and began to separate into two layers, the upper one of chloroform, and the lower of brown oil, which soon began to crystallise. After keeping for a few hours, the crystals were separated from oil and chloroform by filtration, and washed with chloroform. The oil and chloroform were then separated, and the chloroform distilled, when a small further quantity of oil remained, which was added to the separated oil.

The crystals were heated for half an hour on the water-bath with a litre of water, when a part remained undissolved, and after keeping overnight, 27 grams of dibromo-4(or 5)-methylglyoxaline, melting at  $210^{\circ}$ , were collected (mother liquor M).

The oil was also heated for half an hour on the water-bath with a litre of water, but no crystals separated on keeping the solution; this was combined with the mother liquor M and fractionally precipitated with ammonia, when successively small fractions, melting at  $205^{\circ}$ ,  $175^{\circ}$ , and  $120-135^{\circ}$ , and 30 grams melting at  $145^{\circ}$ , were obtained. On evaporating the ammoniacal liquor to low bulk, a further quantity of 35 grams of crystals, melting at  $145^{\circ}$ , separated; 33 grams of brown oil, which became partly crystalline, were obtained by extracting the mother liquor with chloroform; and a further 9 grams of brown oil were similarly extracted after the addition of aqueous sodium carbonate.

The various products were worked up as follows. The fractions

which melted above  $200^{\circ}$  gave, on recrystallisation from ethyl acetate, pure dibromo-4(or 5)-methylglyoxaline, m. p.  $215-216^{\circ}$  (corr.); those melting at  $145^{\circ}$ , after recrystallisation from the same solvent, gave pure bromo-4(or 5)-methylglyoxaline, m. p.  $154-155^{\circ}$  (corr.). The mother liquors, after the removal of ethyl acetate and also those precipitated fractions which were obviously mixtures, were again separated by fractional dissolution in dilute hydrochloric acid and fractional precipitation with ammonia; in this way a further partial separation into crude dibromo-derivative melting at about  $205-210^{\circ}$ , crude bromo-derivative melting at about  $135-145^{\circ}$ , and intermediate fractions, was effected. On crystallisation of these fractions from ethyl acetate, further quantities of the pure compounds were obtained, and the residues were again subjected to the same cycle of operations.

The oil extracted by chloroform from the ammoniacal solution was extracted with water, which removed a quantity of 4(or 5)-methylglyoxaline, and, after fractional treatment with acid and alkali, gave further small quantities of the di- and mono-bromo-derivatives; the 9 grams of brown oil extracted by chloroform after the addition of sodium carbonate were nearly pure 4(or 5)-methylglyoxaline, and crystallised on keeping.

The total yield amounted to 36 grams of pure dibromo-4(or 5)-methylglyoxaline and 67 grams of pure bromo-4(or 5)-methylglyoxaline; there were also obtained 25 grams of viscid, dark brown, partly crystalline oil, which was not further purified, and about 18 grams of nearly pure unchanged 4(or 5)-methylglyoxaline.

The bromination has been carried out at various temperatures with the view of determining the best conditions for the production of the mono-bromo-derivative, with the following result:

One hundred grams of 4(or 5)-methylglyoxaline brominated at

5 to $10^{\circ}$	gave 52 grams of dibromo- and 58 grams of monobromo-derivative
-4 to $-7^{\circ}$	46 " " 62 " " "
-10 to $-12^{\circ}$	36 " " 67 " " "

These figures refer, of course, to the quantities of pure compounds isolated; in each case there was also a dark brown, sticky residue, which could not readily be further purified, and some unchanged 4(or 5)-methylglyoxaline.

It should be mentioned here that when the bromination is carried out at  $5^{\circ}$  to  $10^{\circ}$  or  $-4^{\circ}$  to  $-7^{\circ}$ , the chloroform solution does not remain clear throughout, but gradually becomes turbid, and eventually crystals separate during the addition of bromine.

*Bromo-4(or 5)-methylglyoxaline* (VIII, VIIIa, IX or IXa, p. 1816).

This base crystallises from ethyl acetate in long, glistening, silky needles, which melt at 154—155° (corr.). It is sparingly soluble in cold water, fairly readily so in boiling water, and readily so in alcohol or ethyl acetate. It is soluble in dilute acids, dilute aqueous sodium hydroxide, or in a large excess of 10 per cent. aqueous ammonia, but not in 10 per cent. aqueous sodium carbonate:

0.1503 gave 0.1655 CO<sub>2</sub> and 0.0443 H<sub>2</sub>O. C=30.0; H=3.3.

0.1004 „ 14.7 c.c. N<sub>2</sub> at 16° and 768 mm. N=17.3.

0.1537 „ 0.1809 AgBr. Br=50.1.

C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>Br requires C=29.8; H=3.1; N=17.4; Br=49.6 per cent.

Aqueous solutions of this compound give with silver nitrate solution a white precipitate of the *silver* salt, which crystallises from boiling water in colourless, silky needles.

A solution of this base in dilute aqueous sodium hydroxide becomes deep orange in colour on the addition of aqueous sodium diazobenzene-*p*-sulphonate.

The *hydrogen oxalate* crystallises from water in colourless, prismatic needles, which begin to sinter at 205°, and decompose at 210° (corr.). It is anhydrous, and is very readily soluble in boiling water, but only moderately so in cold water:

0.1532 gave 0.1628 CO<sub>2</sub> and 0.0404 H<sub>2</sub>O. C=29.0; H=3.0.

C<sub>4</sub>H<sub>5</sub>N<sub>2</sub>Br, C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires C=28.7; H=2.8 per cent.

*Dibromo-4(or 5)-methylglyoxaline* (X or Xa, p. 1816).

This compound crystallises from ethyl acetate in glistening, prismatic rods, which melt at 215—216° (corr.). It is almost insoluble in cold water, sparingly soluble in hot water, readily soluble in alcohol, and somewhat sparingly so in ethyl acetate. It is soluble in excess of dilute acids, and readily soluble in aqueous sodium hydroxide or 10 per cent. aqueous ammonia, but not in 10 per cent. aqueous sodium carbonate:

0.1489 gave 0.1111 CO<sub>2</sub> and 0.0261 H<sub>2</sub>O. C=20.3; H=2.0.

0.1516 „ 15.8 c.c. N<sub>2</sub> at 21° and 764 mm. N=11.9.

0.1490 „ 0.2351 AgBr. Br=67.1.

C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>Br<sub>2</sub> requires C=20.0; H=1.7; N=11.7; Br=66.7 per cent.

Aqueous solutions of this compound give with silver nitrate solution a white precipitate of the *silver* salt.

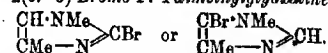
A solution of this base in dilute aqueous sodium hydroxide becomes deep orange in colour on the addition of aqueous sodium diazobenzene-*p*-sulphonate.

*Methylation of Bromo-4(or 5)-methylglyoxaline.*

Seventy grams of bromo-4(or 5)-methylglyoxaline were suspended in 300 c.c. of 10 per cent. aqueous sodium hydroxide, and well shaken while kept cold in running water with 14 grams of methyl sulphate, yielding a nearly clear solution. Quantities of 100 c.c. of 10 per cent. aqueous sodium hydroxide and 14 grams of methyl sulphate were added four times more, so that the total amounts used for the methylation were 700 c.c. of 10 per cent. aqueous sodium hydroxide and 70 grams of methyl sulphate. The addition of these quantities was carried through in one hour, and the mixture well shaken for ten minutes after the last addition.

The oil which had separated was then collected, and the aqueous liquor completely extracted with chloroform; the oil and chloroform were then mixed, dried with anhydrous potassium carbonate, and the solvent distilled. The chloroform residue amounted to 66 grams of brown oil, representing the mixed isomeric *N*-methyl derivatives. The mother liquor gave no more oil on re-methylation. The oil (66 grams) was combined with a similar product (44 grams) obtained by the methylation of another 50 grams of bromo-4(or 5)-methylglyoxaline, and kept overnight in a vacuum desiccator, when a quantity of 2(or 4)-bromo-1:5-dimethylglyoxaline separated in large, flat needles; this was collected, and amounted to 25 grams. The crystals and the oily liquor from which they separated were separately converted into the hydrogen oxalates, and crystallised from water; from the former a quantity of 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate was readily obtained in pure condition (m. p. 146—147°); from the latter, however, various crops of mixed hydrogen oxalates of the two isomerides, melting between about 85° and 95°, were obtained, and these were subjected to a prolonged fractional crystallisation from water. It was found that, on crystallising a mixture melting at about 90° from rather less than its own weight of water, fairly pure 2(or 5)-bromo-1:4-dimethylglyoxaline hydrogen oxalate, melting at 93—95°, would separate in large crystals on keeping overnight, and that the mother liquor, on scratching, would deposit a certain amount of crude 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate as a crystalline powder, melting at about 140°. Eventually, there were obtained altogether (from 110 grams of the mixed isomerides) 84 grams of pure 2(or 5)-bromo-1:4-dimethylglyoxaline hydrogen oxalate, melting at 95—97°, and 12 grams of the same salt in a fairly pure state, also 55 grams of pure 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate, melting at 146—147°, and 8 grams of the same salt in a moderately pure state, together with 10 grams of residues.

## 2(or 5)-Bromo-1: 4-dimethylglyoxaline,



This base was obtained, after regeneration from the pure hydrogen oxalate and extraction with ether, as an oil, which gradually solidified. It crystallises from anhydrous ether in beautiful, clear, colourless, quadrilateral plates, which melt at 40–45° (corr.), after sintering from about 35°.

The base is very deliquescent, readily taking up water, and forming an oil which is sparingly soluble in water. It is not more soluble in alkalis than in water, but is readily soluble in dilute acids. It is readily soluble in alcohol, ether, or chloroform:

0.2076 gave 0.2636 CO<sub>2</sub> and 0.0725 H<sub>2</sub>O. C = 34.6; H = 3.9.

0.1769 „ 0.1908 AgBr. Br = 45.9.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br requires C = 34.3; H = 4.0; Br = 45.7 per cent.

The *hydrochloride* crystallises from water in clear prisms, which, after drying at 100°, melt at 196–197° (corr.). It is very readily soluble in water or alcohol, but very sparingly so in acetone. Its aqueous solution reacts strongly acid:

0.1633 \* gave 0.1681 CO<sub>2</sub> and 0.0567 H<sub>2</sub>O. C = 28.1; H = 3.9.

0.2314 \* „ 0.1583 AgCl. Cl = 16.9.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br.HCl requires C = 28.4; H = 3.8; Cl = 16.8 per cent.

The *hydrogen oxalate* crystallises from water in large, irregular prisms, which melt at 95–97° (corr.), and contain one molecule of water of crystallisation. After drying, first in a vacuum and then at 100°, it melts at 133–135° (corr.). This salt is very readily soluble in hot water, and soluble in less than two and a-half times its weight of water at 25°:

0.1516 † gave 0.1659 CO<sub>2</sub> and 0.0533 H<sub>2</sub>O. C = 29.8; H = 3.9.

0.1611 † „ 13.5 c.c. N<sub>2</sub> at 20° and 760 mm. N = 9.6.

0.2093 † lost 0.0137 at 100°. H<sub>2</sub>O = 6.5.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br.C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O requires C = 29.7; H = 3.9; N = 9.9;

H<sub>2</sub>O = 6.4 per cent.

0.1440 \* gave 0.1688 CO<sub>2</sub> and 0.0457 H<sub>2</sub>O. C = 32.0; H = 3.6.

0.1834 \* „ 0.1293 AgBr. Br = 30.0.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br.C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires C = 31.7; H = 3.4; Br = 30.2 per cent.

The *picrate* crystallises from boiling water in long, flat, yellow needles, which melt at 223–224° (corr.), after sintering earlier. It is very sparingly soluble in water:

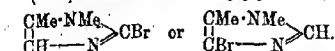
0.1534 gave 0.1835 CO<sub>2</sub> and 0.0362 H<sub>2</sub>O. C = 32.6; H = 2.6.

C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>Br.C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires C = 32.7; H = 2.5 per cent.

\* Dried at 100°.

† Air-dried salt.

## 2(or 4)-Bromo-1: 5-dimethylglyoxaline,



This base crystallises from ether in colourless, transparent splinters (or plates), which melt at 77—78° (corr.). When moistened with water, it becomes oily, and on the addition of a large quantity passes into solution. It is not more soluble in alkalis than in water, but dissolves readily in dilute acids. It is readily soluble in the usual organic solvents, with the exception of light petroleum:

0.1551 gave 0.1941 CO<sub>2</sub> and 0.0596 H<sub>2</sub>O. C=34.1; H=4.3.

0.1517 „ 0.1917 CO<sub>2</sub> „ 0.0584 H<sub>2</sub>O. C=34.5; H=4.3.

0.1683 „ 22.3 c.c. N<sub>2</sub> at 13° and 770 mm. N=15.9.

0.1493 „ 0.1615 AgBr. Br=46.0.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br requires C=34.3; H=4.0; N=16.0; Br=45.7 per cent.

The *hydrochloride* crystallises from moist acetone in rectangular leaflets, which contain about half a molecular proportion of water of crystallisation, and melt at 93—94° (corr.). After drying at 100°, this salt melts at 172—174° (corr.). It is very readily soluble in water or alcohol, but sparingly so in acetone. Its aqueous solution reacts strongly acid:

0.2020 † lost 0.0106 in a vacuum over H<sub>2</sub>SO<sub>4</sub>. H<sub>2</sub>O=5.2.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br.HCl.½H<sub>2</sub>O requires H<sub>2</sub>O=4.1 per cent.

0.1569 \* gave 0.1614 CO<sub>2</sub> and 0.0582 H<sub>2</sub>O. C=28.1; H=4.2.

0.1912 \* „ 0.1296 AgCl. Cl=16.8 per cent.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br.HCl requires C=28.4; H=3.8; Cl=16.8 per cent.

The *hydrogen oxalate* crystallises from water in magnificent, diamond-shaped, transparent plates, which melt at 146—147° (corr.). This salt is anhydrous. It is very readily soluble in hot water, and soluble in four times its weight of cold water:

0.1489 gave 0.1743 CO<sub>2</sub> and 0.0494 H<sub>2</sub>O. C=31.9; H=3.7.

0.1808 „ 16.0 c.c. N<sub>2</sub> at 20° and 767 mm. N=10.2.

C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>Br.C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> requires C=31.7; H=3.4; N=10.6 per cent.

The *picrate* crystallises from water in long, yellow needles, which melt at 198—199° (corr.), after sintering earlier. It is very sparingly soluble in water:

0.1518 gave 0.1830 CO<sub>2</sub> and 0.0346 H<sub>2</sub>O. C=32.9; H=2.6.

C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>Br.C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub> requires C=32.7; H=2.5 per cent.

\* Dried at 100°.

† Air-dried salt.



*Methylation of Dibromo-4(or 5)-methylglyoxaline.*

Fifty-five grams of dibromo-4(or 5)-methylglyoxaline were dissolved in 140 c.c. of 10 per cent. aqueous sodium hydroxide, and well shaken with 15 grams of methyl sulphate (half the calculated quantity), added in small quantities with thorough stirring and cooling under the tap. The solution began to deposit crystals shortly after the first addition of methyl sulphate; these were collected at the end of the methylation, and amounted to 24 grams. The mother liquor, after re-methylation with 90 c.c. of 10 per cent. aqueous sodium hydroxide and 15 grams of methyl sulphate, afforded another 20 grams of crystals, and the final mother liquor, when again methylated with the same quantities, gave a further 8 grams. The total yield of the mixed isomerides was therefore 52 grams, and each crop behaved in the same way on heating, sintering at 75°, and melting at 90—100. The mixture was separated by distillation with steam, when 2: 5-dibromo-1: 4-dimethylglyoxaline passed over very readily, and separated as a colourless oil, which solidified on cooling, and melted at 44—45°. As the distillation proceeded, a small quantity of colourless needles also separated in the receiver, and contaminated the oil, raising the melting point of the solidified oil somewhat; on redistilling with steam, however, the pure low melting isomeride again passed over first. The aqueous distillates still contain a considerable amount of this substance, but the bulk of it may be recovered by distilling these liquors, when it pastes over quickly and largely separates from the first fraction; the remainder may be recovered by extraction with ether. The yield of 2: 5-dibromo-1: 4-dimethylglyoxaline amounted to 20·2 grams.

The residue of the steam distillation, consisting of 2: 4-dibromo-1: 5-dimethylglyoxaline, was purified by crystallisation from ethyl acetate, when it was obtained in beautiful, long, flat needles, which melted at 128—129° (corr.), and in quantity amounting to 20·1 grams.

The separation of the two isomerides may also be effected by crystallisation of the mixture from ethyl acetate; thus, 41 grams of the mixture (m. p. 90—100°), crystallised from 80 c.c. of ethyl acetate, gave at once 9·7 grams, melting at 125°, and, on concentrating, in various crops, 10·9 grams melting between 115° and 123°, then 1·5 grams melting at 90—100°; after removing the solvent from the mother liquor, an oil was obtained; this became solid, melted at 40—46°, and amounted to 17 grams.

By crystallisation of the fractions of high melting point from ethyl acetate, 18 grams of pure 2: 4-dibromo-1: 5-dimethylglyoxaline, and by distillation of the fractions of low melting point

with steam, 13 grams of pure 2:5-dibromo-1:4-dimethylglyoxaline were obtained.



This compound crystallises from light petroleum in flat, prismatic rods, which sinter from 42° and melt at 44—45° (corr.).

It is very easily volatile with steam, sparingly soluble in water, and very readily soluble in the usual organic solvents. It is soluble in dilute acids, but not in alkalis:

0.1516 gave 0.1325 CO<sub>2</sub> and 0.0322 H<sub>2</sub>O. C=23.9; H=2.4.

0.1546 „ 14.3 c.c. N<sub>2</sub> at 16° and 763 mm. N=10.8.

0.1034 „ 0.1538 AgBr. Br=63.3.

C<sub>5</sub>H<sub>6</sub>N<sub>2</sub>Br<sub>2</sub> requires C=23.6; H=2.4; N=11.0; Br=63.0 per cent.

2:4-Dibromo-1:5-dimethylglyoxaline,  $\begin{array}{c} \text{CMe} \cdot \text{NMe} \\ | \\ \text{CBr} - \text{N} \end{array} \gg \text{CBr},$  has previously been described by Jowett and Potter (*loc. cit.*). It melts at 128—129° (corr.), and is soluble in 10 per cent. hydrochloric acid; it is only slightly volatile with steam.

The relative affinity of the two isomeric dibromodimethylglyoxalines has been roughly determined as follows.

0.5 Gram of each isomeride was separately dissolved in 10 c.c. of 10 per cent. aqueous hydrochloric acid, and each solution well shaken with 25 c.c. of chloroform. The chloroform extracts were filtered through a dry filter and evaporated to dryness. In the case of 2:5-dibromo-1:4-dimethylglyoxaline, the chloroform residue amounted to 0.05 gram, melting at 44—45° (corr.), that is, 10 per cent. of the quantity of base present; whilst in the case of 2:4-dibromo-1:5-dimethylglyoxaline, the chloroform residue amounted to 0.31 gram, melting at 128—129° (corr.), that is, 62 per cent. of the quantity of base present.

#### *Bromination of 1:4-Dimethylglyoxaline.*

Three grams of 1:4-dimethylglyoxaline were dissolved in 6 c.c. of chloroform, cooled with ice, and treated with a solution of 6 grams of bromine made up to 5 c.c. with chloroform added drop by drop in ten minutes with thorough stirring. On keeping, the red liquor remained clear; it was shaken with ammonia and water, dried with anhydrous potassium carbonate, and the solvent removed.

The residual oil was dissolved in just sufficient 10 per cent. aqueous hydrochloric acid, diluted, and distilled with steam; the first 30 c.c. of distillate carried over 0.1 gram of 2:5-dibromo-1:4-dimethylglyoxaline as an oil which solidified on keeping, and

collected at 42–44°, a further 70 c.c. of clear distillate were collected, mixed with the 30 c.c. of distillate from which the solid had been separated, and redistilled, when a further 0.09 gram of the same dibromo-compound was obtained.

The acid liquor was then rendered alkaline, and again distilled with steam; the distillate, however, was quite bright even at the commencement, indicating that no considerable amount of the dibromo-compound was contained in the liquor. The liquor was then completely extracted with chloroform, giving 2.7 grams of brown oil; this was converted into the hydrogen oxalate and crystallised from water, when 3.0 grams of 2(or 5)-bromo-1:4-dimethylglyoxaline hydrogen oxalate, melting at 93–94°, separated; after recrystallisation from water, this salt melted at 95–97° (corr.).

#### *Bromination of 1:5-Dimethylglyoxaline.*

Three grams of 1:5-dimethylglyoxaline were brominated with 5 grams of bromine under the same conditions as its isomeride. The resulting orange-red liquor in this case deposited crystals on keeping, but these were not separated, the mixture being extracted several times with water to remove easily soluble hydrobromides.

The chloroform solution was then shaken with dilute ammonia, dried, and distilled, when 2.8 grams of 2:4-dibromo-1:5-dimethylglyoxaline were obtained as a buff, crystalline residue, melting at 127°; after recrystallisation from ethyl acetate, this compound melted at 128–129° (corr.).

The base regenerated from the aqueous extract of the chloroform solution amounted to 1.2 grams, and formed a pale brown oil; this was converted into the hydrogen oxalate, and twice recrystallised from water, when 0.3 grams of 2(or 4)-bromo-1:5-dimethylglyoxaline hydrogen oxalate, melting at 146–147° (corr.), were obtained.

The author wishes to take this opportunity of thanking Dr. Jowett, not only for his introduction to this subject, but also for his kind advice and interest throughout the investigation.

THE WELLCOME CHEMICAL WORKS,  
DARTFORD, KENT.

## CXCVI.—A Glucoside from *Tephrosia purpurea*.

By GEORGE CLARKE, jun., and SHRISH CHANDRA BANERJEE.

*Tephrosia purpurea* (Pers.)—nat. ord. *leguminosae*—a small, woody annual, is found all over India from the Himalayas to Ceylon, and in Assam, ascending to altitudes of 4000 feet.

Native works on *Materia Medica* describe the plant as deobstruent, diuretic, and useful in certain febrile attacks common in the East. When collected for medicinal purposes, the whole plant is gathered just before flowering, dried, and tied in bundles, for sale (Watt, *Dictionary of the Economic Products of India*, Vol. VI, 1893, 15). The *Pharmacographia Indica* states that it contains resin, wax, and a yellow principle allied to quercetin or quercitrin. The latter has not been separated or examined. Owing to the similarity of *Tephrosia purpurea* and the cultivated varieties of the *Indigoferae*, it is known in the vernacular as "jungli nil"—wild blue or wild indigo—although it does not contain any indican or other substance yielding indigo.

Ten lbs. of sun-dried leaves, collected in the Cawnpore district at the end of August, were extracted with cold 95 per cent. alcohol for seven days. The alcoholic extract was drained off as completely as possible, and evaporated to a small bulk under atmospheric pressure. The green extract was poured into water, and washed with light petroleum until the green colour disappeared. The dark brown mother liquor deposited a copious crop of yellow crystals. The yield was about 2½ per cent. of the weight of dry leaves.

The crude substance was best purified by crystallisation from dilute acetic acid (1:3), and finally from dilute alcohol (1:1) or water. It crystallised in yellow needles, soluble in ethyl or methyl alcohols or acetic acid, very sparingly so in cold water, and insoluble in benzene, petroleum, or ether. It dissolved readily in dilute alkalis, giving a yellow solution, from which it could be precipitated by careful neutralisation with mineral acids. It began to sinter at 182°, and finally melted and decomposed at 184–186° (uncorr.).

The pure compound contained water of crystallisation, to which it clung very persistently under atmospheric pressure, and under these conditions required heating to 160° before the last traces of moisture could be expelled. It is easily obtained in an anhydrous state by heating in a vacuum at the boiling point of ethylene dibromide (131°).

The air-dried substance gave on analysis the following results:

0.698 lost 0.058  $H_2O$  in a vacuum at  $131^\circ$ .  $H_2O=8.30$ .  
 0.222 „ 0.0182  $H_2O$  „ „  $131^\circ$ .  $H_2O=8.19$ .  
 0.9552 „ 0.0777  $H_2O$  at  $160^\circ$ .  $H_2O=8.13$ .  
 1.6222 „ 0.1300  $H_2O$  „  $160^\circ$ .  $H_2O=8.01$ .

$C_{27}H_{30}O_{16} \cdot 3H_2O$  requires  $H_2O=8.13$  per cent.

The anhydrous substance is very hygroscopic, and regains water of crystallisation on exposure to air:

0.2650 gained 0.023.  $H_2O=8.67$ .

$C_{27}H_{30}O_{16}$  requires  $H_2O=8.85$  per cent.

Separate fractions of the air-dried substance crystallised from water or dilute alcohol gave on analysis the following results:

0.2138 gave 0.3780  $CO_2$  and 0.1100  $H_2O$ .  $C=48.22$ ;  $H=5.71$ .

0.1810 „ 0.3210  $CO_2$  „ 0.0911  $H_2O$ .  $C=48.36$ ;  $H=5.59$ .

$C_{27}H_{30}O_{16} \cdot 3H_2O$  requires  $C=48.79$ ;  $H=5.42$  per cent.

The anhydrous substance, dried in a vacuum at  $131^\circ$ , gave the following results:

0.2040 gave 0.396  $CO_2$  and 0.0956  $H_2O$ .  $C=52.94$ ;  $H=5.20$ .

0.2136 „ 0.4180  $CO_2$  „ 0.0974  $H_2O$ .  $C=53.37$ ;  $H=5.06$ .

$C_{27}H_{30}O_{16}$  requires  $C=53.11$ ;  $H=4.91$  per cent.

As the substance appeared to be a glucoside, it was examined in the following way. A solution of 20 grams in 1 litre of 2 per cent. sulphuric acid was digested at the boiling point for six hours. As the reaction proceeded, a yellow, crystalline precipitate separated out, and more was deposited on cooling. After being kept overnight, this substance was separated and examined. It was soluble in alkalis, giving a deep yellow solution, and yielded orange-coloured acid derivatives by treating in boiling acetic acid with concentrated hydrochloric, hydrobromic, hydriodic, or sulphuric acids.

The sulphate prepared in this way, washed with acetic acid and dried at  $100^\circ$  until constant in weight, was decomposed by water, and the sulphuric acid estimated:

0.343 gave 0.2004  $BaSO_4$ .  $S=8.02$ .

1.135 „ 0.659  $BaSO_4$ .  $S=7.97$ .

$C_{15}H_{10}O_7 \cdot H_2SO_4$  requires  $S=8.00$  per cent.

The acetyl derivative, prepared from acetic anhydride in the usual manner, and crystallised from ethyl alcohol, melted at  $190-191^\circ$  (uncorr.). After being dried at  $100^\circ$ , it gave the following results on analysis:

0.2070 gave 0.4424  $CO_2$  and 0.0760  $H_2O$ .  $C=58.28$ ;  $H=4.07$ .

$C_{25}H_{20}O_{12}$  requires  $C=58.59$ ;  $H=3.90$  per cent.

The properties of this substance and the analysis of its derivatives left no doubt that it was quercetin.

The filtrate from which the quercetin had been separated was neutralised with barium carbonate, filtered, and evaporated to small bulk on the water-bath under atmospheric pressure. The solution examined in the polariscope was dextrorotatory. It was kept for some days in a partial vacuum over sulphuric acid, but gave no signs of crystallisation.

One gram of the dried syrup in 5 c.c. of water was mixed with 2 grams of phenylhydrazine hydrochloride and 4 grams of sodium acetate in 15 c.c. of water, and heated on the water-bath for three to four hours. Bright yellow crystals separated, which were washed with water and dried in the air. The melting point of the phenylosazone thus produced was  $190-192^{\circ}$  (uncorr.). When crystallised from dilute ethyl alcohol (1:1), it melted indefinitely, at  $190-195^{\circ}$ , but when crystallised from pure ethyl alcohol the melting point was  $206-207^{\circ}$ , and this was not changed when the substance was mixed with *d*-phenylglucosazone.

Ten grams of the phenylosazone were prepared in the manner indicated above with specially purified phenylhydrazine hydrochloride. When fractionally crystallised from ethyl alcohol, it separated into two osazones. The sparingly soluble one melted at  $206-207^{\circ}$  (uncorr.), and the readily soluble one at  $178-180^{\circ}$  (uncorr.). The two substances were recrystallised three times each from ethyl alcohol. Their melting points remained unchanged. They differed in appearance, the fraction of higher melting point consisting of long, silky needles, characteristic of *d*-phenylglucosazone; the more readily soluble fraction crystallised in rosette-shaped clusters of small needles.

Pure phenylrhamnosazone prepared from pure rhamnose melted at  $180-181^{\circ}$  (uncorr.), and the melting point of a mixture of equal quantities of this substance and the readily soluble osazone from the *Tephrosia* glucoside sugars melted at  $178-180^{\circ}$ .

There is thus a very sharp separation into the two phenylosazones of rhamnose and dextrose resembling that described by W. Will in characterising the sugars of hesperidin and naringin (*Ber.*, 1887, 20, 1186).

Somewhat prolonged heating is necessary in preparing the mixed osazones, as phenylrhamnosazone appears to be formed more slowly than the corresponding dextrose derivative.

*d*-Phenylglucosazone (the sparingly soluble osazone), m. p.  $206-207^{\circ}$ , when dried at  $100^{\circ}$  gave the following results on analysis:

0.151 gave 0.3328  $\text{CO}_2$  and 0.0861  $\text{H}_2\text{O}$ . C = 60.10; H = 6.33.

0.2694 „ 0.593  $\text{CO}_2$  „ 0.1515  $\text{H}_2\text{O}$ . C = 60.03; H = 6.24.

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{N}_4$  requires C = 60.33; H = 6.14 per cent.

1836 A GLUCOSIDE FROM *TEPHROSIA PURPUREA*.

Phenylrhamnosazone (the readily soluble osazone), m. p. 178—180°, when dried at 100° gave on analysis the following results:

0.1971 gave 0.4537 CO<sub>2</sub> and 0.1182 H<sub>2</sub>O. C=62.77; H=6.68.

C<sub>18</sub>H<sub>22</sub>O<sub>8</sub>N<sub>4</sub> requires C=63.16; H=6.43 per cent.

A solution of the sugars from the hydrolysis of 20 grams of the pure glucoside from *Tephrosia purpurea*, from which quercetin and sulphuric acid had been separated in the manner described in the preceding experiments, was evaporated to 500 c.c., and cleared with a little washed animal charcoal. The colourless solution thus produced was treated with a few grams of ordinary brewer's yeast for four days at 35—40°. Active fermentation ensued, and a strong odour of alcohol was produced. After separating the yeast, the solution was evaporated to small bulk on the water-bath under atmospheric pressure, and finally dried in a vacuum over sulphuric acid. A few crystals were formed, but not enough to separate. The syrupy residue was warmed with 300—400 c.c. of ethyl alcohol, and a white, flocculent substance, which separated out on the addition of alcohol, was removed. The clear alcoholic solution was evaporated to about 50 c.c., and set aside to evaporate at room-temperature for a few days. About 2 grams of large, rhombic crystals, characteristic of rhamnose, were obtained, and a second crop of smaller crystals separated from the mother liquor.

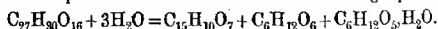
The substance thus produced melted when carefully heated at 33—94° (uncorr.). The melting point of pure rhamnose under the same conditions was 93—94°, and a mixture of equal quantities of pure rhamnose and the rhamnose from the *Tephrosia* glucoside also melted at that temperature.

The rhamnose from the *Tephrosia* glucoside, dried in a vacuum over sulphuric acid, gave on analysis the following results:

0.1866 gave 0.2710 CO<sub>2</sub> and 0.1310 H<sub>2</sub>O. C=39.60; H=7.80.

C<sub>6</sub>H<sub>14</sub>O<sub>6</sub> requires C=39.56; H=7.69 per cent.

The decomposition of the glucoside into quercetin, rhamnose, and glucose takes place in accordance with the following equation:



The decomposition was carried out quantitatively, the quercetin collected in a Gooch crucible, and dried at 160°:

0.544 air-dried glucoside gave 0.246 C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>=45.22.

C<sub>27</sub>H<sub>30</sub>O<sub>16</sub>·3H<sub>2</sub>O requires C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>=45.48 per cent.

0.639 anhydrous glucoside gave 0.315 C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>=49.29.

C<sub>27</sub>H<sub>30</sub>O<sub>16</sub> requires C<sub>15</sub>H<sub>10</sub>O<sub>7</sub>=49.50 per cent.

Two substances have been described which closely resemble the *Tephrosia* glucoside, namely, osyritrin (*Osyris compressa*) and rutin,

which is present in rue (*Ruta graveolens*) and other plants. Whereas the former,  $C_{27}H_{30}O_{16} \cdot 3H_2O$ , gives quercetin and dextrose (Perkin, Trans., 1897, 71, 1134), the latter, originally considered by Schunck (Trans., 1888, 53, 264) to yield only quercetin and rhamnose, has been found by Schmidt (*Arch. Pharm.*, 1908, 246, 214) to have the formula  $C_{27}H_{30}O_{16} \cdot 3H_2O$ , and to give, when hydrolysed, quercetin, rhamnose, and dextrose. Through the kindness of Mr. A. G. Perkin, a small sample of rutin was available for comparison, and as a result of experiment it was found that the *Tephrosia* glucoside is identical with this substance. On the other hand, it is interesting to note that Perkin (private communication) has found that osyritrin is identical with rutin [this vol., p. 1776].

The authors desire to express their thanks to the Managers of the Royal Institution of Great Britain for kindly placing the equipment of the Davy-Faraday Research Laboratory at their disposal for completing this investigation, which was begun in India; and to Mr. H. Martin-Leake, Economic Botanist to the United Provinces Government, for kindly identifying and growing the material used.

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RESEARCH LABORATORIES,  
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## CXCVII.—*Cupricitrates*.\*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

AN examination of the double carbonates of copper and sodium (Trans., 1909, 95, 1409) led to the suggestion that in those of them wherein the copper is electronegative, it is present in the quadrivalent condition as  $:Cu:O$ , united directly with one  $\frac{1}{2}$  of the carbon atoms. The change of the copper atom into such a position from that which it usually occupies would be brought about by the conversion of a carboxyl group into two hydroxyls through the action of an alkaline hydroxide ( $\beta$ -compounds) or carbonate ( $\alpha$ -com-

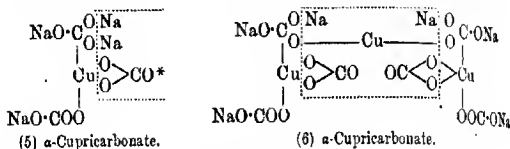
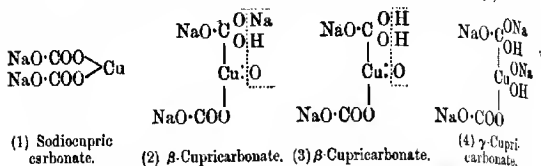
\* Some time has elapsed since this paper was communicated to the Society (see Proc., 1910, 26, 17), and portions of it have been so much elaborated by further work, that it has been considered advisable to reserve these for independent treatment.

† It was originally represented as being united to both the carbon atoms; but this was unnecessary, and involved the somewhat unacceptable assumption of the

group  $:C \begin{smallmatrix} O \\ \diagup \diagdown \\ O \end{smallmatrix}$  being present in the molecule.



pounds), the component atoms of which become added to those of the double salt, as indicated by the formulæ (1), (2) and (5):



The  $\gamma$ -cupricarbonate was not mentioned in the paper itself, but some evidence was given that the action of an alkali could be carried a step further than the formation of the  $\beta$ -compound (2), the copper, as well as the carbon, becoming hydroxylised, and being then in the "cuprite" condition; and it appears now, as was suggested in an addendum to the paper, that it was the  $\gamma$ , and not the  $\beta$ -compound, which was present in the deep violet solution obtained, and described as containing the latter, since there was a large excess of sodium hydroxide present with it. This colour, as well as the property of combining with cellulose, appears to be characteristic of copper in the cuprite condition. Some facts have already been mentioned (*loc. cit.*, p. 1427) to show that a simple sodium cuprite may be obtained by the action of sodium hydroxide on copper oxide, and, also, that calcium cuprites exist.†

The double carbonate, or sodiocupric carbonate, is obtainable as a crystallised salt, but none of the cupricarbonates were isolated, and the evidence in favour of their existence has now been greatly strengthened by the isolation of numerous similar compounds in the case of citric acid. The two cases seem to be very strictly similar; double salts of analogous composition, exhibiting very

\* This group was originally represented as  $\text{C} \begin{array}{c} \text{O} \\ \text{O} \end{array} \text{O}$ , implying the direct union of oxygen atoms, which is now obviated.

† It would be preferable, in the writer's opinion, to adhere to the designation of cuprates, formerly applied, for salts derived from cupric oxide, rather than to reserve that term for the hypothetical derivatives of  $\text{CuO}_2$ . That the latter are red in colour, can scarcely be accepted, as maintained by Ramsay (190, 26, 18), on the strength of Brauner and Kuzma having obtained a red "Tephrosia," which was "supposed to contain a tellurocupric acid" (*Ber.*, 1907, 40).

Similar properties, form the starting point in both series, and the final products of the action of alkalis are in both cases violet compounds, which oxidise dextrose in the cold, and combine with cellulose; whilst, in the case of citric acid, the existence of compounds containing potassium in the condition, both of hydroxide and of carbonate, has been established, by these being isolated in the crystalline condition, and several other similar salts, containing copper in the place of the alkali metal, have been prepared.

In two particulars a modification of the views expressed as to the constitution of the cupricarbonates is suggested by the results obtained with the citrates. Firstly, that the  $\alpha$ -compound is probably not formed by the combination of a molecule of the alkaline carbonate with a molecule of the double carbonate, as shown in (5), but by the combination of a molecule of sodiocupric carbonate with two molecules of the double carbonate, as shown in (6). Its empirical formula would, thus, be  $3[\text{Na}_2\text{Cu}(\text{CO}_3)_2]$ ; and that it does consist of sodium and copper carbonates combined in equal molecular proportions is in accordance with the fact (*loc. cit.*, pp. 1418, 1425) that it is formed in maximum quantity when the reagents are present in such proportions. It may also be mentioned that what appears to be an analogous compound containing potassium has been isolated as a crystalline salt. Secondly, that the substance present in the solution from which the double salt is obtained is really a cupricarbonate, with its copper in the electronegative condition, which renders it possible to attribute the formula for sodiocupric carbonate (1) to the crystallised salt, instead of having to have recourse to the view that it is merely a molecular compound.

The cupricitrates described below are, with one exception, in which the substance is of a constitution different from that in other cases, characterised by certain general features. Unless the proportion of copper present in them is very large, they are all extremely soluble, dissolving in about a third of their weight of water at  $8^\circ$ . The solutions are of an intense blue colour, though of a dirtier tint than that of copper sulphate; they can be concentrated by heat, without decomposition, until a scum begins to form on the very viscous liquid; but crystallisation often does not begin for many days, and proceeds very gradually throughout several days more, until the whole becomes solidified, unless this is prevented by the addition of a little more water. Concentration of the liquid can be effected by adding alcohol. The crystals are microscopic in size, of a dead, somewhat light blue colour, and soft; on filtration from the liquid they form a putty-like mass, and can be purified by recrystallisation only with great difficulty. They

gradually dry at 100° to an extremely hard mass, but most of them retain some water at this temperature, which they give up at 140—150°. The anhydrous compounds are blue and hygroscopic. On heating to a higher temperature they decompose quietly, this affording a convenient means of analysing them, the copper being determined gravimetrically as oxide, and the potassium volumetrically as carbonate.

*Electronegative Copper.*

The presence of a deep blue electronegative ion containing copper was proved in the case of the cupricarbonate by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, 14, 174), and in the case of the cupritartrate by Masson and Steele (*Trans.*, 1899, 75, 725): the apparatus devised by the latter—consisting of two tubes connected by a side-tube filled with agar agar in brine—has been used by the present writer for examining the cupricitrates, and it has been found that they, also, contain a dark blue, slow-moving, electronegative ion, although, during the electrolysis, a certain amount of a light blue, more rapidly-moving, electropositive ion makes its appearance, and results in a deposition of some copper on the negative plate. Copper in the electronegative condition does not, apparently, attack metallic iron, or react with ferrocyanide; but with the latter reagent, the electronegative copper appears gradually to be converted into electropositive, the red colour appearing in a space of time varying between a few seconds and many hours. None of the cupricitrates, except the one containing potassium in the alkaline condition, fail to react with ferrocyanide on long keeping; but that is not the case with certain other cupric compounds examined; potassium cuprisaccharate, for instance, although quite neutral, gives no trace of red with ferrocyanide, unless the solution has been previously boiled, but the boiled solution loses its power of reacting after the lapse of two days.

When no red ferrocyanide is formed—which is also the case if alkali hydroxide is present, either free or as an integral part of the salt—the liquid, if dilute, turns yellow, then green, and, after a long time, an orange precipitate, or ring at the surface of the liquid, forms, which is insoluble in acid, but dissolves in strong alkalis, being first converted by them into a blue substance. Excess of ferrocyanide is required for the formation of this compound.

The presence of free or combined carbonate does not interfere with the formation of the red copper ferrocyanide.

*Compounds Obtained.*

(1) *Potassiccupric Citrate*,  $(C_6H_5O_7)_2CuK_4$ .—When 100 grams of potassium citrate  $(C_6H_5O_7K_3 \cdot H_2O)$  are dissolved in a small quantity of water on a water-bath with 8 grams of citric acid and 40 grams of copper citrate—which is a basic salt,  $(C_6H_5O_7)_2Cu_3 \cdot CuO \cdot 2H_2O$ —the liquid becomes converted into a mass of minute, irregular, hexagonal crystals, which, unlike the cupricitrates, are hard and gritty, and often adhere strongly to the dish. This substance continually makes its appearance when the reagents are taken in proportions other than those mentioned above, and also when no citric acid figures amongst them. It is of a very light blue colour, and although it dissolves to a large extent in water to form a deep blue solution—100 c.c. of a solution at  $8^\circ$ , containing 44 grams of the salt—it does so only very slowly, the result of which is that, when a stream of water is directed on to it on a filter, the moist blue substance becomes white wherever the water falls, and then gradually resumes its blue colour; a behaviour which renders it easily recognisable.

After drying over sulphuric acid or at  $100^\circ$ , various preparations of it gave as a mean:

Found: Cu, 10.56; K, 25.95; Ratio, 1 : 4.00.

Calculated: Cu, 10.63; K, 26.15; Ratio, 1 : 4.

This salt, consisting of two molecules of potassium citrate with two of the potassium atoms displaced by a copper atom, is analogous to the double carbonate of potassium and copper, and, as in the case of the citrate, the substance can hardly be represented as a molecular compound—the constitution of which would have to be  $4C_6H_5O_7K_3 + 3[(C_6H_5O_7)_2Cu]$ —the presumption is that the carbonate also is not a molecular compound. The nature of the two substances, and the similarity of their behaviour with water, gives further support to this view; as they are both light blue, crystalline substances, which in solution form very dark blue liquids.

That these liquids cannot be mere dissolutions of the crystallised substances is demonstrated in the case of the carbonate by the fact that the crystals will not redissolve in the mother liquor, and are decomposed by water. The liquids, it is suggested, contain a cupricompound, formed by the addition of the elements of water to the double salt in a manner similar to that in which the alkaline  $\beta$ -cupricompound is formed by the addition of the elements of  $KHO$ ; the citrate would thus be

(2) A  $\beta$ -cupricitrate,  $(C_6H_5O_7)_2K_4H_2CuO$ , with a constitution similar to that represented by the structural formula (3), p. 1838.

The objection to such a view is that the copper in the dissolved substance appears to be in the electropositive condition, reacting completely with ferrocyanide at once, or very nearly so; this, however, has been proved to be due to the electronegative copper being in a very labile condition, for, on electrolysis, it is found that the copper, or the greater part of it, is really present in the electronegative ion, just as in the case of the other cupricitrates. It is also found that it has the same colour intensity and peculiarities as the copper in these other cupricitrates, this intensity being eighteen times that of the copper in copper sulphate (p. 1850). In the case of the cupricarbonate, the presence of electronegative copper was similarly demonstrated, even in those solutions which contained no excess of sodium carbonate, and the reaction of which with ferrocyanide had previously led to the conclusion that the copper in them must be electropositive (Trans., 1909, 95, 1419).\*

(3) *Potassium  $\beta$ -cupricitrate*,  $(C_6H_5O_7)_2K_4HKCuO$ , has not been isolated with certainty. On one occasion a small crop of microscopic, but comparatively large, crystals was obtained, which were strongly alkaline, and contained no carbonate; these were probably the compound in question, but they were not obtained in quantity sufficient for analysis. On mixing potassiocupric citrate with the requisite amount of potassium hydroxide, and concentrating by exposure over sodium hydroxide—an alkaline solution cannot be concentrated by heat, as copper oxide is thereby separated—a clear, deep blue, and almost solid syrup was obtained, which was still strongly alkaline. After some months, during which a little water had been added several times to it, and the liquid re-evaporated, it gradually became converted into a crystalline magma, which was quite neutral, and consisted probably of a mixture of some of the cupricitrates described below.

(4) *Potassium  $\beta$ -Cupricitrate*,  $(C_6H_5O_7)_2K_6Cu, 6H_2O$ .—Luff obtained this salt by mixing potassium hydroxide, copper sulphate, potassium citrate and citric acid, and concentrating by shaking up with alcohol (*Zeitsch. Ges. Brauwesen*, 1898, 21, 319). Jeffers, who, however, has not published his results, improved the method by substituting copper acetate for the copper sulphate. A still simpler procedure is to dissolve 40 grams of copper citrate in a hot, nearly saturated solution of 100 grams of potassium citrate, and to add to it, when the liquid has cooled to 40–50°, 20 grams of potassium

\* It appears probable that some of the simple copper salts of organic acids may have, in solution, a constitution similar to that suggested for the double citrate in solution. It is remarkable that copper acetate does not act on iron. Salts of iron exhibit like peculiarities; thus, ferric citrate, when quite neutral, gives no reaction with ferrocyanide.

hydroxide in very strong solution. A copious crystallisation occurs, either at once, or on cooling, the crystals consisting of hexagonal tablets, generally very large, clear and regular, and of a fine violet-blue colour. They may be washed with a little water or alcohol, dried between blotting paper, and then by heating at  $100^{\circ}$  for a short time. The substance cannot be recrystallised, as in strong solution it soon decomposes, although in a dilute solution (containing about 0.1 per cent. of copper) it is quite stable, even on boiling. It is insoluble in a strong solution of potassium citrate. It loses a little water very slowly at  $100^{\circ}$ , and  $6\text{H}_2\text{O}$  at  $120$ – $160^{\circ}$ , forming a lavender-coloured mass, which redissolves in water, producing a solution identical in every respect with that obtained by dissolving the hydrated crystals. At  $170^{\circ}$  it becomes green, and on dissolution forms what is apparently a green solution, but this colour is due to the presence of minutely divided cuprous oxide, which eventually subsides, leaving a blue liquid. A similar decomposition occurs with other similar cupric compounds, and has been misinterpreted in several cases as indicating the formation of some substance which is really green.

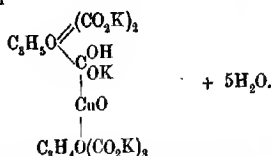
It has no action on metallic iron, and gives no red coloration with ferrocyanic<sup>2</sup>, but the orange substance, mentioned above, is gradually formed if the ferrocyanide is in excess. It does not oxidise dextrose in the cold, but when boiled with it for a few minutes, cuprous oxide is precipitated, which redissolves slowly after cooling.

Many preparations of the salt were analysed, and all gave concordant results, the mean of which was:

Found: Cu, 8.09; K, 29.74;  $\text{H}_2\text{O}$ , 14.10; Ratio, 1 : 5.97 : 6.15.  
Calculated: Cu, 8.13; K, 29.99;  $\text{H}_2\text{O}$ , 13.82; Ratio, 1 : 6 : 6.

This salt has been accepted as being potassium citrate with copper substituted for the hydrogen of the alcoholic hydroxyl; but such a constitution is quite inadmissible, for it is found that the potassium present in it is in two different conditions, one of the six atoms being present as alkaline hydroxide. The alkalinity was determined with sulphuric acid, using phenolphthalein as indicator, and evaporating the liquid repeatedly until the residue showed no further red colour on the addition of water: the mean result of many determinations gave 0.94K as being in the alkaline condition. The only formula that appears capable of expressing this fact is the following, in which the copper functions as in the case of the other cupricitrates, but also acts partly by displacing the hydrogen atom in one of the alcoholic hydroxyl groups, the formation of such a compound being explained by the addition of  $2\text{KOH}$  to the molecule of potassio-cupric citrate, instead

of 1KOH only, as in formula (2), p. 1838, which, resulting as it would in the formation of the unstable group  $\text{Cu} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ , gives rise to rearrangement, with the liberation of the elements of water, and the formation of

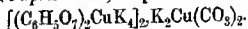


An objection to this formula is that it represents the presence of only five molecules of water of crystallisation, so that, of the six lost on drying, one must be derived from the elements composing the body of the molecule. This is not very improbable, for on dehydration at a temperature a little above  $100^\circ$ , the water lost was found to be considerably less than  $6\text{H}_2\text{O}$  ( $5.3$  to  $5.7\text{H}_2\text{O}$  in various cases), indicating that all the water present is not on the same footing. In any case, however, no argument based on the apparent water contents can counterbalance that depending on the alkalinity of part of the potassium in the salt.

In solution, this salt shows a colour intensity similar to that of the other cupricitrates, but its colour in the solid condition, as well as the size, hardness, and general appearance of the crystals, differentiates it entirely from the latter.

Bullnbeimer and Seitz (*Ber.*, 1900, **33**, 817) obtained a salt which they represent as consisting of two molecules of Luff's salt combined with one molecule of a similar salt with  $\text{K}_2$  in place of  $\text{Cu}$ ; but no details respecting it were published, and the writer has not at present succeeded in preparing it.

(5) *Potassium  $\alpha$ -Cupricitrate*; empirical formula,



—When a concentrated solution of potassium carbonate is added to copper citrate dissolved in potassium citrate, some carbon dioxide is evolved, and, on evaporation, a mass of microscopic, acicular crystals is eventually obtained. They are alkaline in reaction, due to the presence of carbonate, not of hydroxide. The copper present is electronegative, as proved by electrolysis, and gives no reaction with ferrocyanide until after about one minute.

Four preparations, made with various proportions of reagents, gave the following values for the anhydrous substance:

	Found.		Calculated.	
	Per cent.	Ratio.	Per cent.	Ratio.
Cu .....	13.82	3.00	13.08	3
K (total) .....	23.34	10.00	26.82	10
K (alkaline) .....	5.51	1.94	5.36	2
CO <sub>2</sub> .....	4.92	1.55	6.04	2

The water present in the specimens, after drying at 100°, was 2H<sub>2</sub>O in one case, and about 6H<sub>2</sub>O in the others.

The proportions of copper, total potassium, and alkaline potassium agree well with a formula similar to No. 6, p. 1838, representing a substance derived from two molecules of potassiccupric citrate united by one molecule of potassiccupric carbonate. The proportion of carbon dioxide is low, 1.55 instead of 2, due apparently to the fact that some of the compound to be next mentioned is always formed with the  $\alpha$ -cupricitrate, and cannot be effectually separated from it by recrystallisation. In a preparation which evidently consisted of a mixture of these two substances, the proportion of alkaline potassium to CO<sub>2</sub> was found to be 1:1.07, which agrees well with the ratio 1:1 required on the view that K<sub>2</sub>Cu(CO<sub>3</sub>)<sub>2</sub> is present in the molecule.

In accordance with this view, it was found that potassiccupric carbonate dissolved easily and completely in a solution of potassiccupric citrate, even when dilute, although the double carbonate is entirely decomposed by water. The product thus obtained in the case of the citrate was not examined; but that obtained in the corresponding case of the tartrate was found to be a substance containing as part of its composition the elements of potassiccupric carbonate, as here indicated. In the case of the citrate, the dissolution of the double carbonate is always attended by the evolution of some carbon dioxide, so that some substance other than the  $\alpha$ -cupricitrate must be formed at the same time, thus creating the difficulty mentioned above in obtaining the  $\alpha$ -cupricitrate pure. With the tartrate there is no such evolution of gas, and no formation of other substances.

The addition of alkali hydroxide to the  $\alpha$ -cupricitrate abstracts carbon dioxide from it, and precipitates a basic citrate (No. 10, p. 1848), which dissolves in excess of alkali, forming a deep violet solution. This action is precisely similar to that occurring in the case of the  $\alpha$ -cupricarbonate.

The  $\alpha$ -cupricitrate often makes its appearance in alkaline liquids which have been exposed to the air. From the liquids, also, which contained much potassium carbonate, were obtained on several occasions large, acicular crystals of K<sub>2</sub>CO<sub>3</sub>.3H<sub>2</sub>O, which are remarkable in being, unlike the dihydrate and anhydrous salt, non-hygroscopic (Morel, *Bull. Soc. franç. Min.*, 15, 7).



(6) *Tetrapotassio-cupric β-Cupricitrate*,  $(C_6H_5O_7)_2K_4Cu_2CuO$ .—On the solidification of solutions of copper citrate in potassium citrate, there was repeatedly obtained a substance closely resembling the α-cupricitrate in general appearance, but very different in crystalline form: the crystals resembled straight hairs with truncated ends, the length of which was often fifty times greater than the breadth. They gradually grew together into rounded masses, projecting considerably above the liquid. Four samples on analysis after recrystallisation gave:

	Cu.	K.	H <sub>2</sub> O at 100°.	Ratio.
Found:	18.83	23.85	5.22	2 : 4.36 : 2.22
Calculated:	17.82	21.92	5.96	2 : 4 : 2

These values are not very satisfactory, as there always seems to be some of the α-cupricitrate present, which cannot be eliminated by recrystallisation. A mixture of these two substances was recrystallised five times, whereby the relative proportion of the α-cupricitrate was greatly reduced, although there was still a considerable quantity of it left. Ascertaining the amount of this from determinations of the alkaline potassium and carbon dioxide present, and deducting the corresponding quantities of copper and potassium from the totals, the composition of the residue was given as:

Found:	Cu, 19.48; K, 23.98; Ratio, 2 : 4.01.
Calculated:	Cu, 18.76; K, 23.03; Ratio, 2 : 4.

The ratio here is satisfactory, and the discrepancy between the found and calculated percentages would be accounted for by a comparatively small error in the water determination.

The constitution of this compound may be represented as that of a β-cupricitrate similar to No. 3, p. 1833, with the hydrogen atoms of the two hydroxyls displaced by an atom of copper. It is probable that this copper is quadrivalent, and that two such molecules are joined together by means of it:



for the whole of the copper in the compound appears to be electro-negative, not acting on iron, and giving no colour with ferrocyanide until one or two minutes after it is added.

This substance may also be obtained by the decomposition of the following compound.

(7) and (8) *Dipotassio-dicupric β-Cupricitrate*,  
 $(C_6H_5O_7)_2K_2Cu_2CuO$ .

—When copper citrate is beaten with a strong solution of potassio-cupric citrate, it dissolves, but in a few minutes the whole gradually solidifies to a light blue, crystalline mass. After a preliminary

washing to remove soluble impurities, this is found to consist of (a) a small quantity of a dense, dark blue, scaly deposit, often adhering firmly to the dish, and only sufficiently soluble to give a faint reaction with ferrocyanide; and (b), a light blue solid, which, on washing with water for many days, yields continuously a solution containing 0.08 to 0.09 per cent. of copper. Analyses of both these solids, and of the solution obtained from (b), all gave the same ratio for the copper and potassium present:

		Ratio.		
		Cu :	K. :	H <sub>2</sub> O.
Dense solid (a) .....	{	3 : 2.06 :	0.47	
Light solid (b) .....	{	3 : 2.04 :	—	
Solution of (b) evaporated .....	{	3 : 2.08 :	—	
	{	3 : 2.13 :	0.92	
	{	3 : 1.99 :	0.82	

The mean results for (a) and (b) gave, for the anhydrous substance:

Found: Cu, 27.29; K, 11.53.  
Calculated: Cu, 28.77; K, 11.80.

The proportion of water found in (a) indicates that the formula should be doubled, as suggested for the compound last described, (8), from which the present substance differs only in having an atom of copper substituted for two atoms of potassium. These latter may be different atoms in the case of the two compounds (a) and (b), thus accounting for the existence of two substances with the same formula. It acts, although very slowly, on iron, and gives some red colour at once with ferrocyanide; the greater part of the copper in it appears, however, to be electronegative, the full depth of colour being developed only on keeping. The colour-intensity of the copper in the solution is about eleven times that of copper in copper sulphate. In all these respects the characteristics of the substance tally with the formula suggested, which represents the presence of both electronegative and electropositive copper (see p. 1850).

The solution of (b) on evaporation leaves a residue which is decomposed by water, the cupricitrate, No. 6,  $(C_6H_5O_7)_2K_4Cu,CuO$ , passing into solution,\* whilst ordinary basic copper citrate remains undissolved. This reaction indicates that the latter substance is really a

(9) *Copper cupricitrate*,  $(C_6H_5O_7)_2Cu_3,CuO$ , forming with the two last-described compounds a series of cupricitrates in which successive pairs of potassium atoms are displaced by copper atoms, with

\* This would probably be the best method for obtaining this compound in a state of purity.

progressive decrease in solubility. The peculiar lavender-blue colour of copper citrate indicates that it is probably not an ordinary basic salt.

(10) The *basic copper citrate*,  $(C_6H_5O_7)_2Cu_3, 4CuO$ , precipitated by the action of alkali hydroxide on the  $\alpha$ -cupricitrate (p. 1845), appears, on the other hand, to be a true basic salt. It is of a pure blue colour, and, unlike the cupricitrates, it loses all its water at  $100^\circ$ , and begins to decompose at  $160^\circ$ .

(11) A *Potassio-cupric  $\beta$ -Cupricitrate*,  $(C_6H_5O_7)_3K_3Cu_2, 2CuO$ .—During the preparation of one of the cupricitrates, another substance was obtained in considerable quantity, consisting of very regular lenticular crystals, which were so small that they could not be resolved except under a high power of the microscope. Unlike any of the other compounds obtained, this substance is decomposed slowly by water, which accounts for the deficiency of potassium found in it on analysis, the sample having been slightly washed:

Found: Cu, 22.38; K, 15.55; Ratio, 4 : 4.64.

Calculated: Cu, 23.25; K, 18.64; Ratio, 4 : 5.

It contained about  $3H_2O$  at  $100^\circ$ , which it lost at  $160^\circ$ , but this could not be determined satisfactorily, as it began to decompose at, or slightly above, this temperature. The substance is probably, as indicated, similar to No. 6, but derived from three, instead of two, citric nuclei; and the existence of such suggests the possibility of there being many more cupricitrates of complex character. By the action of water on it, a nearly insoluble residue was obtained, which was found to be the cupricitrate No. 8, whilst a blue solution was obtained containing copper and potassium in the ratio of 1 : 3, but whether in the form of a definite compound, or not, was not determined.

(12) *Potassium  $\gamma$ -Cupricitrate*.—Attempts to isolate the deep violet substance present in solution, when excess of alkali is added to any of the cupricitrates, failed. The liquid decomposes with the liberation of cupric oxide when concentrated, either by heat, or by exposure over sulphuric acid. Alcohol abstracts the excess of alkali from it, and Luff's salt is the only product obtained. The colour intensity of the copper in it is about eighty times that of copper in copper sulphate, but increases with the strength of the solution, and with the proportion of alkali added. As regards its colour, the precipitation of cuprous oxide from it by dextrose in the cold, and its combination with cellulose, it is closely similar to what has been described as the  $\gamma$ -cupricarbonate, as well as to other compounds (cupritartrates, etc.) obtained under like conditions.

(13) *Potassio-cupric Hydrogen Citrate*,  
 $(C_6H_5O_7)_2K_4Cu, C_6H_5O_7KH_2, H_2O$ .

—On several occasions the residual liquid after the crystallisation of some of the cupri-compounds, was of a light, greenish-blue colour, especially when citric acid had been taken as one of the reagents, and, on further evaporation, yielded a crop of fairly large, light green, hard crystals, with an acid reaction. They were stable in air, and began to decompose at 150°. On analysis, after drying at 100°, they gave values agreeing with the formula given above, which represents a molecular compound of potassio-cupric citrate with monopotassium citrate:

Found: Cu, 7.34; K, 23.29; Ratio, 1 : 5.04.  
Calculated: Cu, 7.51; K, 23.10; Ratio, 1 : 5.

There is no reason for regarding this salt as a cupri-compound.

#### *The Constitution and Colour of Cupri-compounds.*

The isolation of so many cupricitrates agreeing in their properties, and, apparently, in their constitution, with the non-isolated sodium cupricarbonates, must lend considerable support to the views put forward as to the nature of the latter, especially when the salts isolated are found to include some in which the potassium is present in the condition of hydroxide and carbonate. A considerable amount of additional evidence has already been obtained, all tending in the same direction. Thus, several potassium cupricarbonates have been isolated in the crystalline condition, and these agree with the formulae suggested for the sodium salts, and are, moreover, closely similar in their general characteristics to the cupricitrates here described. According to the views hitherto accepted, the cupricitrates would be represented, either as ordinary copper compounds with the metal displacing the carboxylic hydrogen, or as compounds with the metal displacing the hydrogen in the alcoholic group; according to the view now suggested, the copper is present in the molecule as  $\text{Cu}^+\text{O}$ , and the molecule contains, for each atom of copper present, the elements  $\text{HHO}$  over and above those present according to the ordinary views. It should be possible, therefore, to settle between the rival theories by determining the molecular weight of the compounds. The smallness of the differences to be measured, and the difficulty in obtaining the cupricitrates in a condition of sufficient purity, has rendered such determinations unsatisfactory in their case; but other similar compounds have now been obtained where such difficulties do not exist, and in every one of these instances, now numbering six, the molecular weight of the substance agrees closely with that required according to the present views.

In cases where a copper atom displaces the hydrogen of the two hydroxyl groups, as in No. 6, the properties of the substance seem to be conclusive against its being represented according to the hitherto accepted views; for according to these it would either be potassio-cupric citrate with  $\text{CuO}$  added on to it—that is, an ordinary basic salt—or potassio-cupric citrate, with copper displacing the hydrogen atoms of the alcoholic hydroxyl groups. Numerous compounds, however, have been obtained with copper in the “alcoholic” portion of the molecule, and these are all essentially different in their nature from this, or any of the other cupricitrates; whilst the extreme solubility of this compound must effectually negative the view that it can be a basic salt.

The accepted theory as to the constitution of cupri-salts affords no explanation of the formation of further products by the action of excess of alkali on them, such as must exist in the deep violet solutions thus obtained ( $\gamma$ -cupri-salts), or of the existence of compounds containing as part of their constitution the elements of alkali carbonates ( $\alpha$ -cupri-salts).

Some interesting further evidence on the subject has been obtained from a study of the colour-intensity of these and other copper salts, to which a brief reference only can be made here. The molecular colour-intensity of copper in salts formed from strong acids has approximately the same value in all cases, and is independent of the concentration of the solution throughout the wide range over which comparison is possible. Taking this intensity as unity, that of copper salts derived from weak acids is much greater, reaching the value of 10 in some cases, and in every instance it diminishes as dilution increases, falling to 2 or 3 in most cases, and sometimes even to 1. With the cupri-compounds, however (Nos. 2, 4 and 6, for instance), the colour phenomena are very indifferent, indicating that the copper present must be in some peculiar condition, for the intensity is as high as 18, and remains constant down to extreme dilution. With the compound No. 7, p. 1846, the colour intensity, although still very high, is less than 18, and diminishes slightly on dilution, this being quite in accordance with the view that it is a cupri-compound, but one containing also some copper in the electropositive condition.

The view that copper may act as a tetrad is not new, although its behaviour as such receives very uncertain support from the existence of the oxide  $\text{CuO}_2$ . The extraordinary facility with which it enters into combination with carbon compounds would receive some explanation if its quadrivalent character is admitted, and its position in the periodic system, which is in any case anomalous, can

afford no argument against such a view. That compounds in which copper is directly united to carbon should be explosive, because copper acetylide, the constitution of which is very uncertain, is such (see Ramsay, *Proc.*, 1910, 26, 19), is an argument which can scarcely carry much weight.

HARPENDEN.

### CXCVIII.—*The Constitution of Basic Salts.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

No class of compounds has proved less attractive to chemists during the last half-century than basic salts; they have been accepted as necessary evils, cropping up where least required, and undeserving of any hypothesis to explain their constitution. They are, perhaps, regarded in a hazy way as being analogous to hydrated salts, although such a view can hardly be maintained, for the chief characteristics of hydrated salts are their solubility and powers of crystallising, whilst basic salts are mostly insoluble and amorphous compounds; in hydrated salts, moreover, the bond of union between the water and the salt is, in all probability, the oxygen atoms, whereas in basic salts it would appear to be the metallic atom. It is significant that no basic salts of univalent metals are known.

The want of interest evinced in these compounds is largely due to the fact that there seems to be no guiding principle governing in their formation, and that, in the large majority of cases, even their composition is a matter of considerable doubt. This may be said without any disparagement of the accuracy of the work on which we have to depend for our knowledge respecting them, for at the time when this work was done, ideas as to what constituted valid evidence of the individuality of a compound were very different from what they are now. Certainly our present neglect of basic salts is not justified by any inferiority in the part which they play in chemical changes; for in many manufactures, in the operations of agriculture, and in geological processes, they evidently play, or have played, a very prominent part, and we can hardly claim a satisfactory knowledge of simple salts until we know something of the numerous progeny of basic salts to which they give rise.

Some light appears to be thrown on the matter by a study of the basic sulphates of copper, in connexion with the facts established

regarding the cupri-salts, for it is found that these basic sulphates gradually pass by successive steps from substances akin to ordinary copper sulphate to others wherein the copper is electronegative, ending with compounds which contain no sulphur at all, and which are, apparently, simple cuprites.

The series of substances formed by adding different proportions of lime-water to copper sulphate have already been described (Trans., 1907, 91, 1989), and additional evidence respecting them

*Substances Precipitated from Copper Sulphate by Lime Water.*

Down to (6) the liquids all contain 0.05 per cent. of copper.

Mols. CuO taken to 1 mol. CuSO <sub>4</sub> .	Substance present.	Vol. of precipitate.	Percentage of copper in solution.		Change in dextrose in cold.	Change in dextrose heated.	Colour change on boiling.	Grams of iron dissolved.
			In water. IV.	In dextrose V.				
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
(2). 0.75	{4CuO, SO <sub>3</sub> } (0.06CaSO <sub>4</sub> )	4.1	0.0023	0.0021	nil	nil	nil	0.0022
0.767	Mixture ...	4.7	0.0012	0.0015	nil	nil	nil	—
0.784	" " ...	5.5	0.0005	0.0003	nil	nil	nil	—
(3). 0.8	{3CuO, SO <sub>3</sub> } (0.25CaSO <sub>4</sub> )	6.5	0	0	nil	nil	nil	0.0003
0.832	Mixture ...	8.3	0	0	nil	Dirty green <sup>1</sup>	—	—
0.807	" " ...	12.9	0	0	nil		—	—
(4). 0.9	{2CuO, SO <sub>3</sub> } 1.3CaSO <sub>4</sub>	17.1	0	0	nil	Dirty green and Cu <sub>2</sub> O deposited <sup>2</sup>	Blackens <sup>3</sup>	0.0002
1.0	Mixture ...	17.3	0	0	Deposited in green in { 8 days 2 " 12 hours 1 " 1 hour		—	0.0004
1.1	" " ...	18.5	0	0			—	—
1.16	" " ...	—	0	0			—	—
(5). 1.2	{10CuO, SO <sub>3</sub> } 3CaO, CaSO <sub>4</sub>	19.3	0	0	Deposited in green in { 24 hours 34 " 24 " 1 hour 1 " 1 hour 1 " 1 hour	Cu <sub>2</sub> O deposited <sup>4</sup>	nil	—
1.25	" " ...	15.6	0	some <sup>5</sup>			nil	—
1.30	" " ...	15.8	0	some <sup>5</sup>			nil	—
1.35	" " ...	18.4	0	some <sup>5</sup>			nil	—
2.0	" " ...	18.0	0	0.0021			nil	—
5a). 3.0	Mixture ...	5.7	0	0.002			Turns violet <sup>4</sup>	—
3.5	" " ...	—	0	—	—	—	—	—
4.0	" " ...	—	0	—			—	—
4.5	" " ...	—	0	0.0001			—	—
(6). 25	(CuO, 2CaO)	—	0	—	—	—	—	—
(7). 50	CuO, 3CaO	—	0	—	—	—	—	—
100	" " ...	—	0	—	—	—	—	—
150	" " ...	—	0	—	—	—	nil	—

\* Not determined.

† That is, all the copper dissolved.

‡ If freshly precipitated, these become greener and denser.

§ Increasing in amount with increase of basicity.

|| The amount of green decreasing, and that of deposited oxide increasing, with increase of basicity.

¶ The blackening increasing to a maximum at No. 4 and then decreasing.

‡ The least and most basic precipitate exhibiting a partial change only.

was given in the Eleventh Report of the Woburn Experimental Fruit Farm. These results have been further elaborated recently, but a summary of them will be sufficient here.

The members are numbered (2) to (7) in the above abbreviated table, and to these must be added two other basic sulphates obtained by other means. The first four contain some loosely

combined calcium sulphate, but the amount is so inconsiderable in the case of the first two members, that its presence may be accidental. The proportions of  $\text{CuO}:\text{CaO}$  in Nos. 6 and 7 are uncertain;  $\text{CuO},3\text{CaO}$  seems to be constant in composition throughout a wide range of proportions of lime-water added, but the existence of  $\text{CuO},2\text{CaO}$  is doubtful; all that is certain is that some compound of the two oxides with less calcium than  $\text{CuO},3\text{CaO}$  must exist, as the precipitate becomes destitute of sulphate before it attains the composition of  $\text{CuO},3\text{CaO}$ . All the liquids after passing No. 4 are alkaline.

Columns III to IX contain details as to the behaviour of the various precipitates obtained by adding increasing amounts of lime-water to the same weight of copper sulphate, the total volume of the mixture being the same in all cases.

When first formed, whatever be the proportions taken, the precipitate is the same in appearance, being bulky, and of a full blue colour; but this soon changes to a light blue in the case of the two lowest sulphates (2 and 3), which, in a few days, become greenish-blue and more dense.

The next two members permanently retain their bulky blue character, and, even after being kept for many months, occupy four and a-half times the space occupied by the same amount of copper in the form of the less basic sulphates. If milk of lime, instead of lime-water, be used for preparing the more highly basic precipitates, they are invariably violet, instead of blue, this colour being, as we have reason to believe, distinctive of a cuprite.

The various members of the series, after precipitation, may be converted one into the other by the addition of more lime, or of more copper sulphate, although the conversion occupies some little time.

In column III is given the relative volume occupied by the various precipitates under similar conditions. This increases rapidly up to  $10\text{CuO},\text{SO}_3$ , remains nearly constant to  $10\text{CuO},\text{SO}_3,3\text{CaO}$ , and after decreasing gradually for some distance, begins to fall rapidly.\* The volume occupied by  $5\text{CuO},\text{SO}_3$  shows that it cannot be a mere mixture of the neighbouring compounds, for such a mixture would occupy 5.1 volumes, instead of 6.5; another series, quoted in the Woburn Report, illustrated this point more forcibly.

From column IV it will be seen that the least basic precipitates are sufficiently soluble in water for the amount of copper in solution to be determined by ferrocyanide; the solubility, however, extends

\* The series quoted in the Woburn Report were less complete, and the rapid decrease was erroneously taken as starting at  $10\text{CuO},\text{SO}_3,3\text{CaO}$ .



considerably beyond this point, as is shown by the fact that the more basic liquids act on iron. Column IX contains the results of strictly comparable experiments wherein iron was left in the mixtures for two days. In this action, copper is first deposited on the metal, and then the solution becomes electrolysed, hydrogen being evolved and oxide of iron formed. This action goes on well beyond the point ( $10\text{CuO},\text{SO}_3$ ) at which the liquids become alkaline.

In more strongly alkaline liquids—beyond  $10\text{CuO},\text{SO}_3,3\text{CaO}$ —the iron gradually becomes dulled by the formation of a white deposit on it, which is probably a ferrite. Lime itself has no such action.

When the liquids containing these precipitates are boiled\* (column VIII), no change takes place with the lower members, beyond that of the solids becoming more compact and green, as they do, also, on long keeping. As the basicity increases, a point is reached where boiling causes blackening of a portion of the precipitates, owing to the liberation of cupric oxide. With further increase in basicity, more of the precipitate blackens, the whole of it doing so at  $10\text{CuO},\text{SO}_3$ ; then the blackening diminishes, and ceases altogether at  $10\text{CuO},\text{SO}_3,3\text{CaO}$ . At a further degree of basicity another change begins, this consisting of the precipitate becoming violet and dense, and eventually a point is reached where boiling again produces no change.

Up to a certain point dextrose has no action, and does not affect the solubility of the basic sulphate in the liquid (columns IV and V); but when a certain basicity is reached, we get, apparently, a direct action (column VI), the precipitates being reduced by the dextrose in the cold. This action is evidenced by the precipitates becoming in part of a dirty green colour, due to the mixture of cuprous oxide with the blue precipitate.

When a further degree of basicity is attained, an action of a totally different character occurs; the copper dissolves in the dextrose solution (column V); this becomes violet, and, after being kept for a certain time, turns yellow, owing to the spontaneous separation of cuprous oxide (column VI). The copper, while dissolved, is electronegative, and is absorbed by cellulose; it is present, no doubt, as cupridextrose.

When the basic sulphates are heated to boiling with dextrose solution, the action begins one stage earlier, column VII; the turning green of the undissolved precipitate occurs as soon as  $5\text{CuO},\text{SO}_3$  is passed, and the next stage consists of this same change, together with the dissolution of some of the precipitate, and the gradual

\* They should have been prepared some time before boiling, or they may behave anomalously.

deposition of an increasing amount of cuprous oxide from the solution: in the last stage the cuprous oxide is deposited entirely from the liquid.

The evidence as to the individuality of the various compounds may be summarised as follows:

(1)  $3\text{CuO}, \text{SO}_3$ .—A greenish-blue precipitate, obtained by boiling copper sulphate solution (Pickering, *Chem. News*, 1883, **47**, 181). Also obtained by Shenstone (*Trans.*, 1885, **47**, 375) in a crystalline condition by heating copper sulphate with a little water in sealed tubes at  $200^\circ$ ; and by Friedel. Cesaro and Buttgenbach found it as a mineral. A series of experiments was made to ascertain whether this, or any less basic sulphate, was formed during the partial precipitation of copper sulphate by lime, but no such indications were obtained.

(2)  $4\text{CuO}, \text{SO}_3, (0.06\text{CaSO}_4)$ .—A light blue precipitate, obtained by adding to copper sulphate alkalis in any quantity up to that sufficient to throw down all the metal; also as a crystalline precipitate by decomposing copper sulphate with an acetate (Pickering, *loc. cit.*); and as a crystalline mineral, bronchontite. It turns green on keeping or heating.

(3)  $5\text{CuO}, \text{SO}_3, (0.25\text{CaSO}_4)$ .—Similar in character to the former. Its appearance coincides with the point (1) at which the copper in solution ceases to be recognisable by the ferrocyanide test (column IV in the table), (2) at which cupric oxide begins to be liberated on boiling (column VIII), and (3) at which cuprous oxide begins to separate when heated with dextrose (column VII). The volumes, also, show that it cannot be a mixture of the higher and lower sulphate.

(4)  $10\text{CuO}, \text{SO}_3, 1.3\text{CaSO}_4$ .—A full blue, bulky precipitate, the composition of which is established by its coinciding with the point at which the liquid becomes alkaline when alkali is added to copper sulphate; also by the action of dextrose in the cold, which, as soon as this point is past, begins to act on the precipitate, liberating cuprous oxide from it (column VI), or, when boiled with it, begins to dissolve some of the copper (column VII). The volumes (column III) also indicate its existence.

(5)  $10\text{CuO}, \text{SO}_3, 3\text{CaO}, \text{CaSO}_4$ .—Composition proved by analyses in former communication, and also as being the point (1) up to which some copper is still in solution, as shown by the action of iron (column IX); (2) at which copper begins to dissolve in dextrose in the cold to form a violet solution, depositing cuprous oxide (column VI), and (3) at which boiling ceases to liberate cupric oxide (column VIII).

According to the analyses previously quoted, the composition of this precipitate remains constant with increasing amounts of lime, till the excess of the latter reaches a certain limit (about the point 5a in the table). The change in volumes (column III) and the results on boiling (column VIII) also indicate that some other, as yet unidentified, compound makes its appearance at this point.

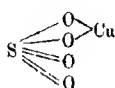
(6)  $\text{CuO}, 2\text{CaO}$ .—Composition uncertain, see above.

(7)  $\text{CuO}, 3\text{CaO}$ .—Approximate composition of the precipitate obtained on adding from 50 to 500 CaO to each molecule of copper sulphate.

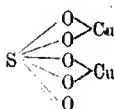
(8)  $15\text{CuO}, \text{SO}_3$ .—A precipitate obtained by decomposing cuprammonium carbonate and sulphate with water (Pickering, Trans., 1909, 95, 1417). Not fully examined.\*

Developing a scheme for the representation of these various substances by the introduction of successive CuO groups into the molecule of copper sulphate, the introduction of one and two such groups gives the members A2 and A3, of which the latter is the lowest basic sulphate known, and is really the orthosulphate, the former being unknown, but analogous to the so-called monohydrate of the sulphate, in which, there can be little doubt, the water is not ordinary water of crystallisation. The introduction of further CuO groups would give the three members of the B series, and of these the first two have been isolated. The members of both these series should all exhibit similar properties, inasmuch as the copper in them is in the same condition. This is the case, for they all react with iron or ferrocyanide, and are not decomposed by dextrose:

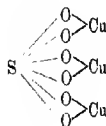
A1.

 $\text{CuSO}_4$ .

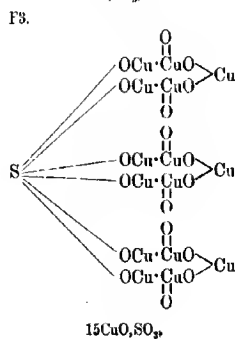
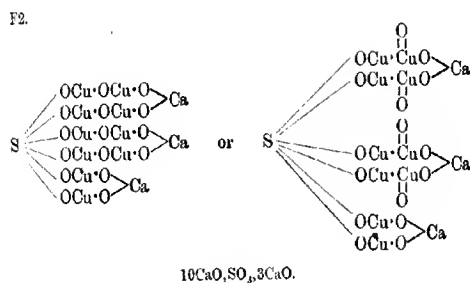
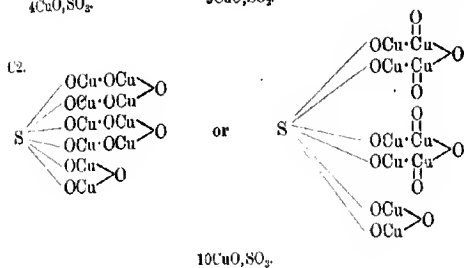
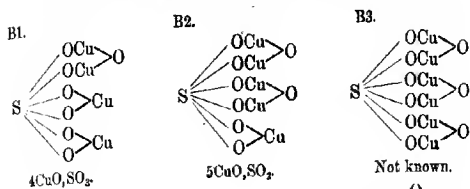
A2.

Not known  
(analogous to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ).

A3.

 $3\text{CuO}, \text{SO}_3$ .

\* It was suggested (Trans., 1907, 91, 1995) that  $10\text{CuO}, \text{SO}_3, 10\text{CaO}, \text{SO}_3$  might exist; this was based on the view, which is now unacceptable, that the higher members of the series were molecular compounds of two basic sulphates of copper and calcium, the compound No. 5 (with the calcium sulphate added to it) being  $10\text{CuO}, \text{SO}_3, 4\text{CaO}, \text{SO}_3$ .



The introduction of further  $\text{CuO}$  groups may be effected in either of the ways indicated in C2, in the first of which the copper is dyad, and in the second, tetrad, as in the case of the cupri-salts. The second member of this series, containing two pairs of such  $\text{CuO}$  groups, corresponds with the next basic sulphate isolated. The ready separation of cupric oxide by heat from this compound (column VIII in the table) would be explained equally well by either of the formulae, but its action on dextrose (column VII), analogous to that of the cupricitrates, seems to be best expressed by the second formula. Its small solubility, and feeble action on iron (column IX) is also more in consonance with this formula, which represents the presence of only one  $\begin{smallmatrix} -\text{OCu} \\ -\text{OCu} \end{smallmatrix} > \text{O}$  group, whereas,

according to the first formula, there are three such groups present, and such a compound would be expected to act at least as energetically as the members of the B series.

By the further action of an alkali, the external  $\text{CuO}$  groups would become converted into "cuprite" groups, as indicated in the alternative formula F2, which represent the next member of the series isolated. Such a substance would be analogous to the  $\gamma$ -cupri-compounds, and, like these, it dissolves in dextrose solution, forming a blue liquid, from which cuprous oxide is deposited (column VII), and which combines with cellulose. The basic sulphate obtained by the decomposition of cuprammonium sulphate fits in as the third member of this series, F3.

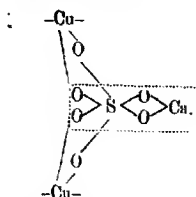
Although the members of the F series are less stable in the presence of dextrose than are those of the preceding series, in consequence of their containing the cuprite groups, they are more stable under the action of heat, the external  $\text{CuO}$  groups being hedged in, as it were, by the outlying electropositive element. The remarkable differences in behaviour of the various basic sulphates on being heated is thus explained.

The series F is derived from the series C by the introduction of  $3\text{M}^{\text{II}}\text{O}$ , and there might be two intermediate series with  $\text{M}^{\text{II}}\text{O}$  and  $2\text{M}^{\text{II}}\text{O}$ , respectively. That some other compounds exist which have not been isolated is almost certain, as has already been pointed out.

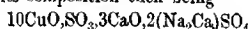
The final products of the action of limo on copper sulphate seem to be simple cuprites, and the oxidising action of these on dextrose is still more energetic than that of highest basic sulphate.

Two members of the sulphate series, C2 and F2, contain a considerable proportion of combined calcium sulphate; the presence of this can be explained if the alternative formulae are adopted, but not otherwise, the calcium sulphate becoming an

orthosulphate by connexion with two  $\text{CuO}$  groups of the quadri-valent copper:



The maximum amount of sulphate thus capable of being introduced would be two molecules, and this is the amount actually found when the basic sulphate F2 is precipitated in the presence of excess of sodium sulphate, its composition then being



(*loc. cit.*).

#### Ferrites.

How far the explanation which seems to be satisfactory with the copper compounds will apply to those of other metals remains to be seen; but, in the case of iron, some evidence has been obtained that an analogy exists.

In a paper on emulsions (*Trans.*, 1907, 91, 2001) it was mentioned that when ferrous sulphate is precipitated by excess of lime, and churned up with paraffin, the greenish-black precipitate of basic sulphate often becomes quite white, or does so when the emulsion is kept for some time. This was attributed to the chemical action of some impurity in the oil; but it has since been found that the same change occurs, although much more slowly, when the basic sulphate is left with milk of lime only, or even with excess of clear lime-water, decolorisation in that case requiring many days to become complete. The white substance retains the flocculent character of the basic sulphate, and remains quite unchanged in a closed vessel, but when exposed to the air it very gradually becomes orange, through the formation of ferroso-ferric oxide. On digestion with a solution of dextrose, a small portion of it dissolves, and in this the iron is in the electronegative condition, as it gives no blue colour with ferrocyanide until acid is added.

To obtain some information on the subject, quantities of one litre of lime-water, diluted with 20 per cent. of water, were mixed with different amounts of ferrous sulphate, and left in closed bottles for six weeks, after which the lime still in solution was determined. In this way the molecular proportions of lime used up

in the precipitation of the iron were determined, and these are given in the accompanying table. The proportions of lime to iron taken are also given, and, as will be seen, the lime in all cases was in excess. It was only in the last three experiments that the greenish-black basic sulphate became white; it very nearly did so in No. 4, whilst in No. 3 there was a smaller, but still considerable, lightening in colour. Taking the last three experiments, where the change was complete, the proportion of lime used up is evidently in excess of the one molecule which would suffice for the complete decomposition of the ferrous sulphate, so that some of the lime must have gone into combination with the ferrous oxide. Omitting the last experiment, as being uncertain owing to the very small proportions in which the iron had to be taken, the excess of lime used is  $0\cdot27\text{CaO}$ , which would indicate the formula of the compound as  $4\text{FeO},\text{CaO}$ , if no sulphur is left in it; this, however, was not the case, for, in No. 5, there was found to be  $0\cdot153\text{SO}_3$  present to each atom of iron, and in No. 6,  $0\cdot05\text{SO}_3$ ; this may be present simply as calcium sulphate, but, if it is combined with the iron in the form of a basic sulphate, the proportions of  $\text{FeO}$  to  $\text{CaO}$  in the precipitate would be less than the 4 : 1 mentioned above.

*Precipitation of Ferrous Sulphate by Lime.*

	Proportions taken. Fe : $\text{CaO}$ .	Proportions used up. Fe : $\text{CaO}$ .
1.	1 : $1\cdot033$	1 : $0\cdot334$
2.	1 : $2\cdot07$	1 : $0\cdot543$
3.	1 : $5\cdot15$	1 : $0\cdot641$
4.	1 : $10\cdot3$	1 : $1\cdot030$
5.	1 : $25\cdot3$	1 : $1\cdot232$
6.	1 : $51\cdot5$	1 : $1\cdot311$
7.	1 : $103\cdot0$	1 : $1\cdot116$

Further work would be required, of course, before the nature of the substances here present could be established, but it is evident that ferrous compounds analogous to the alkaline basic salts of copper or to the cuprites do exist, and it is noticeable that their formation seems to necessitate approximately the same large excess of alkali, for with the iron compound between 10 and 26 equivalents of lime to each equivalent of iron are required, whilst in the case of copper, about 25 equivalents were necessary (*loc. cit.*).

The solubility of basic metallic salts of this description in organic substances probably plays an important part in their assimilation by plants. \*

HARPENDEN.

INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1911. 1861

The Council has ordered the following letter and report to be printed in the Journal and Proceedings of the Society:

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,  
SOUTH KENSINGTON,  
LONDON, S.W.  
August 22nd, 1910.

GENTLEMEN,

I beg to forward the Annual Report of the International Committee on Atomic Weights for 1911, to which I have appended, by their desire, the signatures of Professors Ostwald and Urbain.

The Committee, it will be seen, have acceded to the wish of the Council of the Chemical Society, and have prepared the Report in such time that it can be published prior to the commencement of the ensuing academic year.

Slight changes have been made in the atomic weights of argon, helium, krypton, lithium, neon, phosphorus, platinum, strontium, vanadium, and x mon, but otherwise the new table remains very much as in 1910.

I have the honour to be, Gentlemen,  
Your obedient servant,  
T. E. THORPE.

To the Hon. Secretaries,  
The Chemical Society,  
Burlington House,  
London, W.

Report of the International Committee on Atomic Weights, 1911.

In the autumn of 1909 the Council of the Chemical Society of London voted unanimously in favour of issuing the annual report of the International Committee on Atomic Weights in September or October instead of in January as heretofore. In that proposition the Chemical Society of France has concurred, and American sentiment has also been favourable to the suggested change. Therefore the change is now made.

The reasons offered for the new policy are very simple. First, the school year, at least in most educational institutions, begins in the autumn. It is desirable that teachers should then have the latest



table of atomic weights at their command, in order to avoid change after school work has begun. Secondly, publishers of text-books are accustomed to issue their new works in the autumn, and often request early information as to changes which are likely to be made. The proposed change in the time of issuing the table is therefore an aid to teachers, students, and publishers, and no disadvantage to anyone else. The immediate usefulness of the table is increased, and to attain that end should be the main purpose of the Committee.

Since the preparation of the report for 1910, a number of important memoirs upon atomic weights have appeared. The results obtained are, in brief, as follows:

*Chlorine*.—The density, composition by volume, and compressibility of hydrochloric acid have been measured by Gray and Burt (Trans., 1909, 95, 1633) with great care. From the density and volumetric composition, when  $H = 1.00762$ ,  $Cl = 35.459$ . From the density and compressibility,  $Cl = 35.461$ . The mean, 35.460, is the value given in the annual table of atomic weights for the past two or three years.

The density of hydrochloric acid has also been determined by Scheuer (*Zeitsch. physikal. Chem.*, 1909, 68, 575), who gives measurements made under varying conditions. His final conclusion, based upon his own work after comparison with that of Gray and Burt, is that  $Cl = 35.466$ .

*Lithium*.—Richards and Willard (*J. Amer. Chem. Soc.*, 1910, 32, 4), in their important research upon the atomic weight of lithium, measured three distinct ratios, namely, silver to lithium chloride, silver chloride to lithium chloride, and lithium perchlorate to lithium chloride. From these ratios, without the intervention of any others, the following independent values for three atomic weights are obtained:

$$Li = 6.939.$$

$$Cl = 35.454.$$

$$Ag = 107.571.$$

The value for silver varies from the accepted value, 107.88, by about one part in 12,000, which is probably less than the actual uncertainty. That for chlorine diverges more widely, namely, by about one part in 6000. The new figures are undoubtedly entitled to great weight, but in view of the excellent work done by others it would be unwise to make any hasty change in the table. For lithium, however, the value 6.94 may be taken, replacing the old 7.00.

*Strontium*.—Thorpe and Francis (*Proc. Roy. Soc.*, 1910, 83, 4,

277), in their determinations of the atomic weight of strontium, measured six ratios, and obtained the following results:

Ratio 2Ag to SrBr <sub>2</sub> .....	Sr=87.645
„ 2AgBr to SrBr <sub>2</sub> .....	„=87.653
„ 2Ag to SrCl <sub>2</sub> .....	„=87.642
„ 2AgCl to SrCl <sub>2</sub> .....	„=87.645
„ SrBr <sub>2</sub> to SrSO <sub>4</sub> .....	„=87.629
„ SrCl <sub>2</sub> to SrSO <sub>4</sub> .....	„=87.661
Mean of all .....	Sr=87.646

The value adopted by the authors is 87.65. Richards's figure is 87.62. An intermediate value, 87.63, is adopted in the new table.

*Phosphorus*.—Atomic weight redetermined by Baxter and Jones (*J. Amer. Chem. Soc.*, 1910, **32**, 298). From the ratio between silver and silver triphosphate, the authors find  $P=31.043$ , when  $Ag=107.88$ . The rounded-off figure 31.04 is to be adopted.

*Vanadium*.—From the ratio between silver chloride and vanadyl trichloride, Prandtl and Bleyer (*Zeitsch. anorg. Chem.*, 1910, **65**, 152) find  $V=50.963$  and 51.133 in two series of experiments. In a later paper, Prandtl and Bleyer (*Zeitsch. anorg. Chem.*, 1910, **67**, 257), also from analyses of vanadyl trichloride, find  $V=51.061$ . From reductions of  $V_2O_5$  to  $V_2O_3$ , they found  $V=51.374$ . The latter method, however, they regard as uncertain. The value  $V=51.06$  may be provisionally adopted.

*Tellurium*.—Marckwald and Foizik (*Ber.*, 1910, **43**, 1710; see also Browning and Flint, *Amer. J. Sci.*, 1909, [iv], **28**, 347, who adduce evidence to show that tellurium is possibly complex), by a somewhat complex volumetric process, based on the oxidation of  $TeO_2$  by  $KMnO_4$ , conclude that  $Te=127.61$ . This agrees with many of the other recent determinations of the constant, but is not sufficiently exact to supplant the value given in the table.

*Rhodium*.—Two inaugural dissertations upon the atomic weight of rhodium have been issued from Gutbier's laboratory at Erlangen. Ranz reduced rhodium pentamine bromide in hydrogen and found  $Rh=102.92$ . H. Dittmar (reproduced in *Sitzungsber. phys. med. Soc. Erlangen*, **40**, 184), by similar reductions of the corresponding chloride, found  $Rh=102.93$ .

*Platinum*.—The very elaborate investigation of Archibald (*Proc. Roy. Soc. Edin.*, 1909, **29**, 721) upon the atomic weight of platinum was based upon analyses of the chloroplatinates and bromoplatinates of potassium and ammonium. In all, 28 ratios were measured, giving values for Pt ranging between 195.19 and 195.25. Their arithmetical mean gives  $Pt=195.22$ . Archibald, however, in his

final discussion, uses only 12 ratios, giving, in mean,  $Pt=195.23$ . The figure 195.2 is given in the table.

*The Inert Gases.*—The densities and molecular weights of helium and neon have been redetermined by Watson (Trans., 1910, 97, 810). For the atomic weights he finds  $He=3.994$  and  $Ne=20.200$ . In another paper (*ibid.*, 97, 833) he applies the critical constants of krypton and xenon to their densities as determined by Moore, and finds  $Kr=82.92$  and  $Xe=130.22$ . There are also new determinations of the density of argon by Fischer and Hehnel (*Ber.*, 1910, 43, 1435). Their mean value, referred to  $O=16$ , is 19.945, a figure rather higher than that given by Ramsay and Travers. It corresponds to an atomic weight of  $A=39.89$ .

It is also to be noted that a third, revised edition of Clarke's "Recalculation of the Atomic Weights" has recently been published by the Smithsonian Institution.

The annual table of atomic weights for 1911 follows, with but few changes from that of the preceding year.

F. W. CLARKE.

W. OSTWALD.

T. E. THORPE.

G. URBAIN.

1911.

*International Atomic Weights.*

O=16.		O=16.	
Aluminium .....	Al 27.1	Molybdenum .....	Mo 96.0
Antimony .....	Sb 120.2	Neodymium .....	Nd 144.3
Argon .....	A 39.88	Neon .....	Ne 20.2
Arsenic .....	As 74.96	Nickel .....	Ni 58.68
Barium .....	Ba 137.37	Nitrogen .....	N 14.01
Bismuth .....	Bi 208.0	Osmium .....	Os 190.9
Boron .....	B 11.0	Oxygen .....	O 16.00
Bromine .....	Br 79.92	Palladium .....	Pd 106.7
Cadmium .....	Cd 112.40	Phosphorus .....	P 31.04
Cesium .....	Cs 132.81	Platinum .....	Pt 195.2
Calcium .....	Ca 40.09	Potassium .....	K 39.10
Carbon .....	C 12.00	Praseodymium .....	Pr 140.6
Cerium .....	Ce 140.25	Radium .....	Ra 226.4
Chlorine .....	Cl 35.46	Rhodium .....	Rh 102.9
Chromium .....	Cr 52.0	Rubidium .....	Rb 85.45
Cobalt .....	Co 58.97	Ruthenium .....	Ru 101.7
Columbium .....	Cb 93.5	Samarium .....	Sa 150.4
Copper .....	Cu 63.57	Scandium .....	Sc 44.1
Dysprosium .....	Dy 162.5	Selenium .....	Se 79.2
Erbium .....	Er 167.4	Silicon .....	Si 28.3
Europium .....	Eu 152.0	Silver .....	Ag 107.88
Fluorine .....	F 19.0	Sodium .....	Na 23.00
Gadolinium .....	Gd 157.3	Strontium .....	Sr 87.63
Gallium .....	Ga 69.9	Sulphur .....	S 32.07
Germanium .....	Ge 72.5	Tantalum .....	Ta 181.0
Glaucium .....	Gl 9.1	Tellurium .....	Te 127.5
Gold .....	Au 197.2	Terbium .....	Tb 159.2
Helium .....	He 3.99	Thallium .....	Tl 204.0
Hydrogen .....	H 1.008	Thorium .....	Th 232.0
Indium .....	In 114.8	Thulium .....	Tm 168.5
Iodine .....	I 126.92	Tin .....	Sn 119.0
Iridium .....	Ir 193.1	Titanium .....	Ti 48.1
Iron .....	Fe 55.85	Tungsten .....	W 184.0
Krypton .....	Kr 82.9	Uranium .....	U 238.5
Lanthanum .....	La 139.0	Vanadium .....	V 51.06
Lead .....	Pb 207.10	Xenon .....	Xe 130.2
Lithium .....	Li 6.94	Ytterbium (Neoytterbium) .....	Yb 172.0
Lutecium .....	Lu 174.0	Yttrium .....	Y 89.0
Magnesium .....	Mg 24.32	Zinc .....	Zn 65.37
Manganese .....	Mn 54.93	Zirconium .....	Zr 90.6
Mercury .....	Hg 200.0		



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## ERRATA.

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- Page Line  
 1297 13\* for " $\text{C}_6\text{H}_5\text{--}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix}\text{--}\text{C}_6\text{H}_4\text{--OH}$ " read " $\text{C}_6\text{H}_5\text{--}\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix}\text{--}\text{C}_6\text{H}_4\text{--OH}$ "  
 1398 4\* ,, "*5-Nitro-6:7-dimethylcoumarin*." read "*5-Nitro-6:7-dimethylcoumarin*."  
 1733 20 ,, "*270°*" read "*240°*."  
 1738 11\* ,, "*Benzoylnaphthyl*" read "*Benzoyl*."  
 1826 2\* ,, "*deep orange*" read "*pale yellow*."

## VOL. XCVIII (ABSTR., 1910).

- i, 214 { 5\* }  
 i, 215 { 2\* } for "*dl-hydroxyerythronic acid*" read "*dl-oxerythronic acid*,"  
 { 3 }  
 { 6 }  
 i, 415 19 ,, "*JULIUS*" read "*JOHANNES*."  
 i, 435 1 ,, "*1-phenyl-3-methyl-5-hydroxymethylpyrazolone*" read "*1-phenyl-3-methyl-5-hydroxymethylpyrazole*."  
 i, 471 21 ,, "*acetyl-p-nitrophenylethyldimethylamine*" read "*acetylphenylethyldimethylamine*."  
 i, 495 6 ,, "*mesodioxathrone*" read "*mesobenzodioxathrone*."  
 i, 500 15\* ,, "*3-oxo-(1)-thiosalicylic acid*" read "*3-oxo-(1)-thionaphthen*."  
 CH — CMe CH — CMe  
 i, 574 16\* for  $\begin{array}{c} \text{CH}_3 \quad \text{C:N-OH} \\ | \quad | \\ \text{C} \text{-----} \text{CH}_2 \\ | \\ \text{CMe}_2\text{OH} \end{array}$  read  $\begin{array}{c} \text{CH}_3 \quad \text{C:N-OH} \\ | \quad | \\ \text{CH} \text{-----} \text{CH}_2 \\ | \\ \text{CMe}_2\text{OH} \end{array}$   
 i, 574 { 10\* } delete commas preceding and following "however."  
 { 9\* }  
 ii, 81 22 ,, "*STZEKI*" read "*SCZEKI*."  
 ii, 162 14 ,, "*1910*" read "*1909*."  
 ii, 501 17\* ,, "*CASTELLANA*" read "*CASTELLANI*."  
 ii, 707 18 ,, "*ii, 557*" read "*ii, 120*."  
 ii, 747 17 ,, "*ALEXANDRON*" read "*ALEXANDROFF*."  
 ii, 793 4\* ,, "*Newton*" read "*Overton*."  
 ii, 796 19\* ,, "*alcapitan*" read "*alcapton*."  
 ii, 799 { 20 }  
 { 24 } ,, "*phymouthiensis*" read "*plymouthiensis*."  
 ii, 838 5\* insert "*sodium*" before "*dihydrogen*."

1911.

*International Atomic Weights.*

O=16.		O=16.	
Aluminium .....	Al 27.1	Molybdenum .....	Mo 96.0
Antimony .....	Sb 120.2	Neodymium .....	Nd 144.3
Argon .....	A 39.93	Neon .....	Ne 20.2
Arsenic .....	As 74.96	Nickel .....	Ni 58.68
Barium .....	Ba 137.37	Nitrogen .....	N 14.01
Bismuth .....	Bi 208.0	Osmium .....	Os 190.9
Boron .....	B 11.0	Oxygen .....	O 16.00
Bromine .....	Br 79.92	Palladium .....	Pd 106.7
Cadmium .....	Cd 112.40	Phosphorus .....	P 31.04
Cesium .....	Cs 132.81	Platinum .....	Pt 195.2
Caesium .....	Cs 132.81	Potassium .....	K 39.10
Calcium .....	Ca 40.09	Praseodymium .....	Pr 140.6
Carbon .....	C 12.00	Radium .....	Ra 226.4
Cerium .....	Ce 140.25	Rhodium .....	Rh 102.9
Chlorine .....	Cl 35.46	Rubidium .....	Rb 85.45
Chromium .....	Cr 52.0	Ruthenium .....	Ru 101.7
Cobalt .....	Co 58.97	Samarium .....	Sa 150.4
Columbium .....	Cb 93.5	Scandium .....	Sc 44.1
Copper .....	Cu 63.57	Selenium .....	Se 79.2
Dysprosium .....	Dy 162.5	Silicon .....	Si 28.3
Erbium .....	Er 167.4	Silver .....	Ag 107.83
Europium .....	Eu 152.0	Sodium .....	Na 23.00
Fluorine .....	F 19.0	Strontium .....	Sr 87.63
Gadolinium .....	Gd 157.3	Sulphur .....	S 32.07
Gallium .....	Ga 69.9	Tantalum .....	Ta 181.0
Germanium .....	Ge 72.6	Tellurium .....	Te 127.5
Glucinum .....	Gl 9.1	Terbium .....	Tb 159.2
Gold .....	Au 197.2	Thallium .....	Tl 204.0
Helium .....	He 3.99	Thorium .....	Th 232.0
Hydrogen .....	H 1.008	Thulium .....	Tm 168.5
Iodine .....	I 126.92	Tin .....	Su 119.0
Iridium .....	Ir 193.1	Titanium .....	Ti 49.1
Iron .....	Fe 55.85	Tungsten .....	W 184.0
Krypton .....	Kr 83.9	Uranium .....	U 238.5
Lanthanum .....	La 139.0	Vanadium .....	V 51.06
Lead .....	Pb 207.19	Xenon .....	Xe 130.2
Lithium .....	Li 6.94	Ytterbium (Neoytterbium) .....	Yb 172.0
Lutesium .....	Lu 174.0	Yttrium .....	Y 89.0
Magnesium .....	Mg 24.32	Zinc .....	Zn 65.37
Manganese .....	Mn 54.93	Zirconium .....	Zr 90.6
Mercury .....	Hg 200.0		



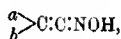
CXCIX.—*Optically Active Salts of 4-Oximinocyclohexanecarboxylic Acid and the Configuration of the Oximino-Group.*

By WILLIAM HOBSON MILLS and ALICE MARY BAIN.

THE theory which Hantzsch and Werner put forward (*Ber.*, 1890, 23, 11) to account for the isomerism of the oximes provides so satisfactory and consistent an explanation of the facts that it has received practically universal acceptance. The fundamental assumption, however, on which this theory is based—namely, that in the oximino-group the three valencies of the nitrogen atom are not in one plane—has rested up to the present on indirect evidence only.

It seemed to us that it might be possible to put this hypothesis to direct experimental test by investigating an oximino-compound so constituted that its molecule would possess a plane of symmetry or not according as the oximino-group has a plane or a trihedral configuration.

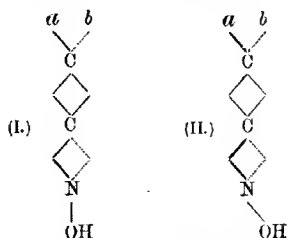
This condition is fulfilled by compounds of the type:



which might be regarded as oximes of the unsymmetrical ketens:

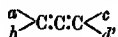


A molecule of the configuration (I) is clearly superposable on its mirror-image, whilst one of configuration (II) is not.

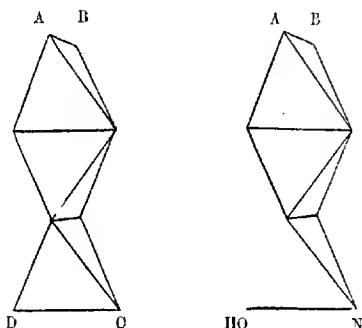


In these diagrams the dotted lines are intended to indicate valencies lying behind the plane of the paper, while valencies in front of it are represented by thick lines.

A substance of configuration (II) stands in close relationship to allene derivatives of the type:

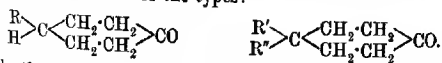


the molecular asymmetry of which was first pointed out by van't Hoff in 1875 (*La Chimie dans l'Espace*, p. 29), for, provided that the oximino-group has the configuration assumed by Hantzsch and Werner, it can be substituted for one of the carbon atoms of such an allene compound, as shown in the diagram, without destroying the asymmetry of the molecule:



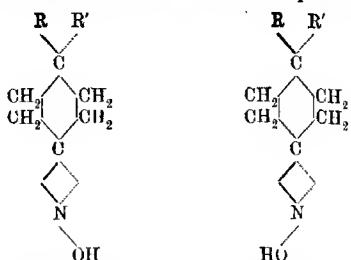
The preparation and manipulation of a compound of this type would doubtless offer even greater difficulties than those which have hitherto prevented the experimental realisation of van't Hoff's prediction in its original form (see Dimroth and Feuchter, *Ber.*, 1903, **36**, 2238; Lapworth and Wechsler, *Trans.*, 1910, **97**, 38).

These difficulties can, however, be avoided by means of the same device as has been successfully employed by Perkin and Pope (*Trans.*, 1908, **93**, 1075; Perkin, Pope, and Wallach, *Trans.*, 1909, **95**, 1789; compare Marckwald and Meth, *Ber.*, 1906, **39**, 1171) in order to obtain a compound (methylcyclohexylidene-4-acetic acid) which reproduces the essential spatial characteristics of the allene derivatives without having their instability—that is, by the expansion of the two-membered ethylene ring into the hexamethylene ring. In place of keten oximes, one then has the oximes of substituted cyclohexanones of the types:



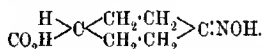
If the three valencies of the nitrogen atom in the oximino-group

are not in one plane, then the oxime of such a ketone must consist of an equimolecular mixture of two enantiomorphous forms:



If, on the other hand, they are in one plane, these oximes, like the ketones from which they are derived, will have a plane of symmetry, and will therefore be incapable of exhibiting optical activity. Hence, if a compound of such constitution can be obtained in an optically active condition, it will follow as a necessary consequence that the three valencies of the nitrogen atom in the oximino-group do not lie in one plane.

In order to facilitate resolution, it is desirable that the substance should contain the carboxyl group. The simplest compound of the necessary type is therefore:



This is the oxime of the important *cyclohexanone-4-carboxylic acid* which was synthesised by W. H. Perkin, jun. (Trans., 1904, **85**, 416), and served as the basis of his well-known syntheses of terpin, terpineol, and dipentene (Trans., 1904, **85**, 654). It has also been obtained by Lumsden (Trans., 1905, **87**, 87) by the reduction of anisic acid. It is shown in the present communication that this oximino-acid (or rather its salts) is, in fact, capable of existing in two enantiomorphously related forms, the separation of which has been effected with the aid of morphine and quinine.

If a molecular proportion of morphine is added to the ethyl-alcoholic solution of the acid, a morphine salt separates which contains a dextrorotatory form of the acid, for on decomposing it with excess of ammonia and suitably removing the morphine, the ammonium salt which remains in the solution is strongly dextrorotatory. The ammonium salt prepared in this manner has a molecular rotation  $[\text{M}]_D$  in aqueous solution varying from about  $50^\circ$  to  $60^\circ$  in different preparations. By means of quinine the corresponding levorotatory ammonium salt has similarly been obtained, the salt which the *l*-acid forms with the alkaloid being in

this case the more sparingly soluble of the two diastereoisomerides. This levorotatory ammonium salt has a molecular rotation of  $[\text{M}]_D -70^\circ$  to  $-80^\circ$  in aqueous solution; the separation effected by quinine is thus more complete than that attained with the aid of morphine. The activity of these salts is evanescent, and its rate of disappearance falls off in accordance with the unimolecular formula, the velocity constants being very different for different salts of the acid. The rate of racemisation is greater, in the salts investigated, the weaker the base from which the salt is derived, and the presence of an excess of alkali, which in so many cases accelerates racemisation, here greatly retards it, while acidification causes the rapid disappearance of the rotatory power. Thus the morphine salt of the *d*-acid when dissolved in water shows mutarotation, obviously on account of the rapid diminution of the dextrorotation due to the acid, the period of half-change being about one minute. For an approximately 0.2*N*-solution of the ammonium salt in water, the time of half racemisation is thirteen minutes, and for the sodium salt under similar conditions twenty-four minutes. The presence of ammonia in *N*/10-concentration increases the persistence of the activity of the ammonium salt approximately forty-fold, raising the period of half-change to 8.5 hours, and a corresponding addition of sodium hydroxide to the solution of the sodium salt has a still greater relative effect on the rate of racemisation, lengthening the period of half-change from twenty-four minutes to twenty-two hours.

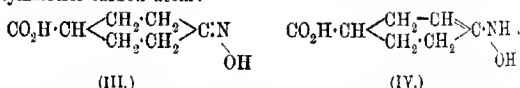
The rapid racemisation of the salts of the acid with weak bases renders intelligible the results observed in preparing the morphine and quinine salts from the inactive acid. In the case of the latter salt, for example, the crystals which separate yield a levorotatory ammonium salt after decomposition with ammonia and removal of the quinine, but there is no corresponding amount of quinine *d*-acid salt in the mother liquor, the solution of ammonium salt, obtained after removal of the quinine from the latter, being quite inactive. However, on concentration of the mother-liquor, another crop of quinine *l*-acid salt is deposited of similar activity to the first, and so on. The behaviour of the morphine salt is analogous—not only the first crystallisation, but also the subsequent crops obtained on concentration of the alcoholic mother liquor all yield solutions of dextrorotatory ammonium salt after removal of the morphine.

The process therefore appears to be one of activation rather than of simple resolution, and recalls the behaviour of the methylethylpropyl tin *d*-camphorsulphonate and bromocamphorsulphonate described by Pope and Peachey (Proc., 1900, 16, 42, 116).

It seemed inevitable from the foregoing that any attempts to

isolate the optically active forms of the acid itself would be unsuccessful. It was therefore necessary, in order to make these experiments as conclusive as possible, to obtain some definite proof that the substances, to which these optically active solutions owe their rotatory power, are indeed the normal ammonium salts of dextro- and lævo-rotatory forms of oximinocyclohexane-4-carboxylic acid. This was done by treating the active solutions with an aqueous solution of silver nitrate. The substances thus precipitated, from the dextro- as well as from the lævo-rotatory solutions, were found to be normal silver salts of this acid in analytically pure condition. Further, they were optically active, for on treating them with an aqueous solution of sodium chloride, the solutions of sodium salt obtained were respectively dextro- and lævo-rotatory, the rotations observed corresponding with molecular rotations  $[M]_D^{25}$  74.5° and -79.9° respectively.

These results show conclusively that the salts of this oxime-acid are capable of existing in two enantiomorphously related forms. Moreover, the evanescent character of the optical activity makes it certain that their molecular asymmetry is determined in some manner by the oximino-group.\* It remains to be considered whether any method of accounting for the asymmetry is possible other than that indicated at the beginning of this paper. Apparently the only other hypothesis by which it might, at first sight perhaps, appear explicable is that the compound can exist in the two tautomeric forms (III) and (IV), and that the optically active salts are derived from the latter, which contains an ordinary asymmetric carbon atom:



This explanation, however, cannot be maintained. If the active compound has the formula (IV), it is a  $\beta$ -substituted hydroxylamine, and must possess the power of reducing Fehling's solution, which is characteristic of compounds of this class. A comparison of the behaviour of an active solution in this respect with that of acetoxime on the one hand, and of  $\beta$ -phenylhydroxylamine on the other, showed that although its reducing power was slightly greater than that of acetoxime, it was of an altogether different order from that of phenylhydroxylamine, and it is quite certain that no appreciable quantity of a  $\beta$ -substituted hydroxylamine could have been present in the solution.

The conclusion therefore seems unavoidable that the molecular asymmetry, to which these salts owe their optical activity, is determined by the peculiar configuration of the doubly linked tervalent

nitrogen atom. They accordingly constitute a new type of optically active substances; and through their optical activity a direct experimental proof is afforded that the three valencies of tervalent nitrogen, however they may be disposed in a compound of the type



are directed in the oximino-group, as was postulated by Hantzsch and Werner, along the three edges of a trihedral angle.

These substances may also possess a certain interest in that they provide another example of compounds of which, like *d*- and *l*-inositol,\* and *d*- and *l*-1-methylcyclohexylidene-4-acetic acids (Perkin, Pope, and Wallach, *loc. cit.*), the molecular asymmetry is more fittingly defined with reference to the configuration of the molecule as a whole than expressed in terms of the presence of some "asymmetric atom."

#### EXPERIMENTAL.

The cyclohexanone-4-carboxylic acid employed for the preparation of the oxime the properties of which form the subject of this communication, was synthesised according to the method described by W. H. Perkin, jun. (*loc. cit.*); and Kay and Perkin (*Trans.*, 1906, **89**, 1640). The acid was converted into its oxime by mixing its solution in ten parts of absolute alcohol with one molecular proportion of hydroxylamine hydrochloride dissolved in about an equal volume of the same solvent, and adding one molecular proportion of anhydrous sodium acetate. After three days an equal volume of dry ether was added, the precipitated sodium chloride was removed, and the solution then evaporated, finally in an exhausted desiccator. The oximino-acid was extracted from the solid residue in a Soxhlet apparatus, and purified by recrystallising from dry ether in the same manner. It separates from ether in crystalline crusts, melting at 148–148.5°, and otherwise agreeing with Perkin's description (*loc. cit.*).

#### *Quinine Salts of Oximinocyclohexane-4-carboxylic Acid.*

A quinine salt containing a preponderance of the levorotatory form of the acid may be obtained by heating the solution of the inactive acid in 30 parts of water with 2.1 parts (slightly more than one molecular proportion) of anhydrous quinine, the small excess of quinine being removed by filtration of the hot liquid. The salt separates on cooling, usually in hemispherical clusters of

\* The configuration of the active inositols was, apparently, first given in *Stereochemie* (van't Hoff-Meyerhoffer, 1892), p. 91; see also Bouveault, *Bull. Soc. chim.*, 1894, [iii], 11, 145.

fine needles. After being air-dried, it contains  $2\frac{1}{2}$  molecules of water of crystallisation:

1.2756 air-dried salt lost  $0.1070 \text{ H}_2\text{O}$ .  $\text{H}_2\text{O} = 8.39$ .

1.0693 " " "  $0.0894 \text{ H}_2\text{O}$ .  $\text{H}_2\text{O} = 8.36$ .

$\text{C}_{27}\text{H}_{35}\text{O}_5\text{N}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  requires  $\text{H}_2\text{O} = 8.56$  per cent.

Under the above conditions, approximately 80 per cent. of the total quantity of salt crystallises out. Recrystallisation can be conveniently effected from 10 parts of hot water.

The investigation of the optical activity of the acid component of the salt was carried out by placing a weighed quantity of the salt (0.3 to 0.5 gram) in a small separating funnel, and adding 10 c.c. of an aqueous solution of sodium or ammonium hydroxide of such concentration that the amount of alkali left after decomposition of the salt would give an approximately  $N/10$ -solution. The quinine was then completely removed by extracting three times with chloroform, 12—15 c.c. of chloroform being used for each extraction. The alkaline solution of the sodium or ammonium salt was then filtered, and after washing the separating funnel and filter with successive small quantities of  $N/10$ -sodium or ammonium hydroxide, as the case might be, the mixed filtrate and washings were examined polarimetrically. For example, 0.66 gram of air-dried quinine salt was treated with an aqueous solution (10 c.c.) of 0.12 gram of sodium hydroxide. After proceeding in the above manner, the following polarimetric observation was made, the final volume of the aqueous solution being 14.00 c.c.:

$$l = 2, c = 1.606, \alpha_D = -1.47^\circ, [\text{M}]_D = -81.9^\circ.$$

On examination of the various preparations of quinine salt in this manner, it was found that the sodium or ammonium salts obtained from them possessed molecular rotations lying for the most part between  $[\text{M}]_D = -70^\circ$  and  $[\text{M}]_D = -80^\circ$ .

It was naturally useless to attempt to obtain the optically pure quinine *l*-acid salt by repeated recrystallisation in the usual way, since it is clear from the observations described below (pp. 1880, 1881) that even with the most rapid working it must be impossible to avoid racemising the salt extensively with regard to its acid component every time that it is brought into solution. The conditions were rather to be sought under which the pure salt would crystallise out directly free from its diastereoisomeride. These should presumably be such as would secure that the rate of racemisation should be a maximum compared with that of crystallisation, since in this manner the concentration of quinine *l*-acid

\* The concentrations given throughout this paper refer to the sodium or ammonium salt present in the solution examined. They are calculated from the amount of quinine or other salt taken.

salt would be kept as high, and that of quinine *d*-acid salt as low as possible during the crystallisation. Accordingly, it was endeavoured to diminish the rate of crystallisation by slow cooling and accelerate that of racemisation by acidification, and, in fact, although the experiments in this direction are not complete, the salt of highest activity (with regard to the acid component) hitherto observed was obtained by crystallisation from a solution somewhat strongly acidified with acetic acid, the sodium salt prepared from it having given the following numbers:

$$l=2, c=0.727, \alpha_D -0.74^\circ, [M]_D -91.0^\circ.$$

In preparing the quinine *l*-acid salt from inactive acid, it is found that the excess of the dextrorotatory form of the acid, which should be present in the mother liquor in order to correspond with the excess of the levorotatory form removed from the solution in combination with quinine, has disappeared, for the mother liquor (at any rate if a short time is allowed to elapse before its separation and examination) contains the quinine salt of the inactive acid only, since after the addition of a small excess of sodium hydroxide solution and removal of the quinine by chloroform, the solution of sodium salt obtained is inactive. On concentrating the mother liquor, the second crop of quinine salt obtained contains again an excess of the *l*-acid salt. For example, after converting 3.2 grams of inactive acid into quinine salt in the manner described above, the crop, which crystallised directly, weighed 8.5 grams (about 80 per cent. of the total quantity of salt produced) and gave rise to sodium salt of molecular rotation  $[M]_D -71.5^\circ$  ( $c=0.731$ ). The second crop, obtained by concentrating the mother liquor, weighed 0.96 gram (another 10 per cent. of the total quantity of salt), and gave rise to sodium salt of molecular rotation  $[M]_D -81.9^\circ$  ( $c=1.607$ ).

These results are clearly due to the racemisation phenomena which have already been mentioned. Of the two diastereoisomeric quinine salts, that of the *l*-acid must be the less soluble in water, and thus crystallises first from an aqueous solution containing equal quantities of the two salts. The excess of quinine *d*-acid salt thereby left in solution, however, racemises very rapidly, so that in spite of the removal of the quinine *l*-acid salt, an approximate equality is maintained between the quantities of the two salts in the solution. An excess of the quinine *l*-acid salt is accordingly deposited throughout the process of crystallisation.

In our earliest experiments (Proc., 1909, 25, 177) the quinine *l*-acid salt was obtained by combining the inactive acid with quinine in ethyl acetate solution and allowing crystallisation to take place from that solvent. This procedure was abandoned, since it was



found that this salt could be obtained more rapidly and certainly, and, moreover, in a state of higher optical activity, by using water as solvent. These experiments were, however, of some interest, since by means of them not only the quinine *l*-acid salt, but also in some cases a salt containing a preponderance of the diastereoisomeric quinine *d*-acid salt was obtained. Thus, in one experiment, 5.4 grams of quinine (anhydrous) were dissolved in 300 c.c. of dry ethyl acetate, and to the boiling solution 2.61 grams (one molecular proportion) of the finely powdered acid were added. The quinine salt formed separated very slowly. After five days it was collected, and a portion dried in a vacuum was polarimetrically examined in solution in ethyl acetate, racemisation taking place in this solvent far more slowly than in water or in alcohol:

$$l = 2; c = 1.6512; \alpha_D^{18} - 3.24^\circ; [\alpha]_D^{18} - 98.1^\circ.$$

Since the specific rotation in ethyl acetate of the quinine salt of the inactive acid (prepared by dissolving 0.2732 gram of anhydrous quinine and 0.1324 gram of the acid in 25 c.c. of ethyl acetate) was found to be as follows:

$$l = 2; c = 1.6224; \alpha_D^{18} - 4.28^\circ; [\alpha]_D^{18} - 131.9^\circ$$

the acid component of the salt was clearly markedly dextrorotatory. On recrystallisation of this preparation from ethyl acetate, some of the dextrorotatory power was, however, lost, the specific rotation having risen to  $[\alpha]_D^{18} - 106.5^\circ$ . The dextrorotatory ammonium salt obtained from this quinine salt was examined with the following result:

$$l = 2, c = 0.947, \alpha_D 0.44^\circ, [\alpha]_D 40.4^\circ.$$

These results recall the interesting observations recently made by McKenzie and Clough (Trans., 1909, 95, 783) on the crystallisation of the morphine salt of phenylchloroacetic acid, a given ethyl-alcoholic solution of morphine (1 mol.) and *r*-acid (2 mols.) depositing either morphino *d*-acid or morphine *l*-acid salt, according to the exact conditions under which crystallisation takes place.

*Silver 1: 4-Oximinocyclohexanecarboxylate.*—To the solution of ammonium *l*-acid salt, obtained by adding a solution of 0.348 gram of ammonia in 14 c.c. of water to 6.61 grams of quinine *l*-acid salt, and removing the quinine by extracting with chloroform, an aqueous solution of 2.75 grams of silver nitrate was added. The dense precipitate of silver salt thus produced was collected, thoroughly washed with water, rapidly passed out on a porous tile, and then dried for five days over sulphuric acid in an exhausted desiccator, the whole of the operations being carried out in non-actinic light. 2.20 Grams of silver salt were thus obtained in the form of a white powder, which apparently can be preserved indefinitely if protected

from light. On being gently heated, it decomposes almost explosively, but if mixed with a large proportion of powdered cupric oxide, its analysis presents no special difficulty:

0.3860 gave 0.4542  $\text{CO}_2$  and 0.1368  $\text{H}_2\text{O}$ .  $\text{C}=32.09$ ;  $\text{H}=3.94$ .

0.2783 „ 13.35 c.c.  $\text{N}_2$  at  $24^\circ$  and 760 mm.  $\text{N}=5.37$ .

0.2978 „ 0.1616  $\text{AgCl}$ .  $\text{Ag}=40.85$ .

$\text{C}_7\text{H}_{10}\text{O}_3\text{NAg}$  requires  $\text{C}=31.82$ ;  $\text{H}=3.79$ ;  $\text{N}=5.30$ ;

$\text{Ag}=40.90$  per cent.

This silver salt is too sparingly soluble to allow of its rotatory power being measured directly. It was, however, possible to demonstrate its optical activity by converting it into sodium salt and determining the rotatory power of the latter. Dry silver salt (0.8901 gram) was digested with 7 c.c. of an aqueous solution of sodium chloride containing 4.4 grams of sodium chloride and 0.4 gram of sodium hydroxide in 100 c.c., the sodium hydroxide being added in order to check the racemisation of the dissolved sodium salt, which proceeds rapidly in neutral solution (see p. 1877). The resulting solution was decanted from the solid residue through a filter, the residue repeatedly extracted in the same way with successive small quantities of the alkaline solution of sodium chloride, and the total filtrate polarimetrically examined:

$l=2$ ,  $c=0.4065$ ,  $\alpha_D -3.82^\circ$ ,  $[\text{M}]_D -79.9^\circ$ .

*Morphine d-Oximinocyclohexane-4-carboxylate*. — When equimolecular proportions of morphine and oximinocyclohexane-4-carboxylic acid are mixed in hot ethyl-alcoholic solution, the sparingly soluble morphine salt which separates contains a preponderance of the dextrorotatory form of the acid. 5.8 Grams of the acid, dissolved in 50 c.c. of absolute alcohol, were added to a hot solution of 11.19 grams of morphine in 200 c.c. of the same solvent. The salt (14.04 grams) was gradually deposited, on cooling, in rosettes of small prisms. It can be recrystallised from about 30 parts of boiling absolute alcohol. It can also be recrystallised from methyl alcohol, but it is very sparingly dissolved by ethyl acetate, chloroform, or other common organic solvents, although easily soluble in cold water. The optical activity of the acid component of the salt was examined in a manner similar to that employed in the case of the quinine salt. The very finely powdered salt was treated with an aqueous solution of so much ammonia as to leave an approximately decinormal solution of the latter after the decomposition of the salt. The separated morphine was then removed by filtration, and washed with successive small quantities of a  $N/10$ -aqueous solution of ammonia. The filtrate and washings were freed from dissolved morphine by repeated extraction with

their own volume of chloroform, and then polarimetrically examined. 2.6 Grams of morphine salt digested with a solution (8.4 c.c.) containing 0.114 gram of ammonia and treated in this manner gave a solution which was examined in the polarimeter with the following result:

$$l=2, c=7.31, \alpha_D 5.43^\circ, [M]_D 64.6^\circ.$$

The salt racemises as regards its acid component very rapidly in alcoholic solution. It is therefore not possible to obtain the more soluble morphine *l*-acid salt from the mother liquor after the crystallisation of the less soluble *d*-acid salt. On concentration of the mother liquor, the crystals which separate still contain an excess of the latter salt. Also, the degree of separation of the two diastereoisomeric salts attained depends greatly on the exact conditions under which crystallisation takes place. Different crops of crystals examined in the manner described above gave ammonium salts of the following molecular rotations:  $[M]_D$  43°, 48°, 64.6°, 50°, 68°, 52°, 53.5°.

*Silver d-Oximinocyclohexane-4-carboxylate.*—Finely powdered morphine salt (6 grams), which had been twice crystallised from alcohol, was treated with an aqueous solution (8.8 c.c.) containing 0.253 gram of ammonia. The separated morphine was removed in the manner already described, and the resulting solution, after having been polarimetrically examined:

$$l=2, c=16.634, \alpha_D 9.57^\circ, [M]_D 50.1^\circ,$$

was treated with an aqueous solution of 2.55 grams of silver nitrate. The silver salt was collected, washed, and dried exactly as in the case of the silver salt of the *l*-acid. It weighed 2.38 grams, and was analysed with the following results:

0.3961 gave 0.4623 CO<sub>2</sub> and 0.1387 H<sub>2</sub>O. C=31.83; H=3.89.

0.4968 „ 21.75 c.c. N<sub>2</sub> (moist) at 14° and 759 mm. N=5.14.

0.4876 „ 0.2652 AgCl. Ag=40.94.

C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>NAg requires C=31.82; H=3.79; N=5.30;  
Ag=40.90 per cent.

A portion of the same preparation (1.0019 grams), on treatment with an alkaline solution of sodium chloride as described in the case of the silver salt of the *l*-acid, gave a solution of dextrorotatory sodium salt, which was polarimetrically examined, with the following result:

$$l=2; c=4.8523; \alpha_D^{15} 2.68^\circ; [M]_D^{15} 49.4^\circ.$$

Dextrorotatory silver salt of higher activity was subsequently obtained from a solution of ammonium salt of molecular rotation  $[M]_D 64.6^\circ$  ( $c=7.31$ ) made from a preparation of morphine salt (2.6 grams), which had been four times recrystallised from alcohol.

On treatment with silver nitrate, this gave 0.917 gram of silver salt, 0.6151 gram of which was converted into sodium salt in the manner described. The rotatory power of the resulting solution was as follows:

$$l=2, c=2.979, \alpha_D 2.48^\circ, [\text{M}]_D 74.5^\circ.$$

*Reducing Power of the Optically Active Sodium Salt.*—For reasons given in the introduction (p. 1870), it appeared desirable to compare the reducing power of an active solution of the sodium salt of the oximino-acid towards Fehling's solution with that of  $\beta$ -phenylhydroxylamine on the one hand and that of acetoxime on the other.

1.62 Grams of quinine *l*-acid salt were treated with a solution (15 c.c.) of 0.2 gram of sodium hydroxide, and the separated quinine was removed by extraction with chloroform. For comparison with the solution of the sodium salt of the *l*-oximino-acid in *N*/10-sodium hydroxide thus obtained, solutions of equimolecular quantities of phenylhydroxylamine (0.37 gram) and of acetoxime (0.246 gram) in 15 c.c. of *N*/10-sodium hydroxide were prepared. The three solutions were respectively added at 20° to three quantities of Fehling's solution, each containing 1 gram of crystallised copper sulphate (1.2 mols.), 5 grams of Rochelle salt, 1.5 grams of sodium hydroxide, and 60 grams of water. The solution to which the phenylhydroxylamine had been added was, of course, completely reduced in a few seconds. The other two were kept well stoppered for twenty-four hours in a thermostat at 20°, and the small quantities of cuprous oxide which had been precipitated in each were collected and their respective amounts determined:

Precipitated by acetoxime: 0.013 gram  $\text{Cu}_2\text{O}$ ; 0.065 atom Cu.

Precipitated by sodium salt of oximino-acid: 0.0316 gram  $\text{Cu}_2\text{O}$ ; 0.132 atom Cu.

The reducing power of the sodium salt of the oximino-acid in alkaline solution is therefore, as was to be expected, of the same order of magnitude as that of acetoxime, and of an altogether different order from that of phenylhydroxylamine. There is therefore no reason to suppose that the hydroxylamine residue contained in these optically active salts possesses a constitution different from that usually assigned to it in the ketoximes.

#### *The Racemisation Phenomena.*

*The Sodium Salt.*—A solution of levorotatory sodium salt free from excess of alkali was prepared by digesting active silver salt with a slight excess of an aqueous solution of sodium chloride. 2.40 Grams of quinine *l*-acid salt (giving sodium salt of molecular

rotation  $[M]_D - 76.3^\circ$ ,  $c = 0.633$ ) were converted into ammonium salt in the manner already described, and the weakly ammoniacal solution of the ammonium salt thus obtained was treated with an aqueous solution of silver nitrate (0.935 gram). The precipitated silver salt, after having been carefully washed free from ammonia, was digested while still moist with an aqueous solution (20 c.c.) of 0.292 gram of sodium chloride. After thirty seconds, the solution of sodium salt thus obtained (which would be approximately 0.2-normal, and would also contain the slight excess of sodium chloride used) was filtered as rapidly as possible from silver chloride and examined in a 2-dcm. tube. The rotation was seen to diminish, the diminution taking place, as is shown in the accompanying table, in accordance with the unimolecular formula. The temperature was  $20.4^\circ$ :

$t$ (mins.).	Rotation.	$1/t \log a/(a-x)$ .
0.0	$-1.44^\circ$	—
2.75	1.34	0.011
5.85	1.22	0.012
10.40	1.08	0.012
15.0	0.94	0.012
20.3	0.80	0.013
25.7	0.67	0.013
35.9	0.51	0.013
47.3	0.36	0.013

Taking 0.0125 as the value of the constant, the period of half-change is twenty-four minutes.

*Sodium Salt in Presence of Sodium Hydroxide.*—The solution on which the observations were made was prepared in the following manner. 2.50 Grams of quinine *l*-acid salt were treated with an aqueous solution (10 c.c.) of 0.246 gram of sodium hydroxide. The liberated quinine was removed with chloroform, and the separating funnel washed with small quantities of  $N/10$ -sodium hydroxide solution. The resulting solution was placed in a 2-dcm. tube, which was kept between the observations in a thermostat at  $20^\circ$ . The rotation was found to be continually decreasing, again in accordance with the unimolecular formulæ, but very much more slowly than in the previous experiment.

$t$ (hours.).	Rotation.	$1/t \log a/(a-x)$ .
0.0	$-3.42^\circ$	—
1.46	3.20	0.0147
3.95	3.00	0.0144
5.66	2.85	0.0140
7.75	2.66	0.0141
9.88	2.49	0.0140
21.62	1.71	0.0139
24.24	1.57	0.0139
26.75	1.44	0.0140
29.75	1.33	0.0138
46.23	0.79	0.0138

Taking the value of the constant to be 0.0139, the time of half-change is 21.7 hours—fifty-four times as great as that for the sodium salt in neutral solution. The concentration of the sodium hydroxide was determined after the polarimetric observations were finished by titrating 10 c.c. of the solution with *N*/10-sulphuric acid, using phenolphthalein as indicator. It was thus found to be 0.098-normal. The concentration of the sodium salt, calculated from the quantity of quinine salt taken, was 0.32-*N*.

*Ammonium Salt*.—An approximately 0.2-*N*-solution of levorotatory ammonium salt was prepared by a method exactly analogous to that employed in the case of the sodium salt. The same quantity of quinine *l*-acid salt (2.4 grams) was converted into ammonium salt (the molecular rotation of which was  $[\text{M}]_D - 72.8^\circ$ ,  $[\alpha]_D = 5.674$ ) and the silver salt obtained from it by precipitation with silver nitrate was digested with a solution of 0.267 gram of ammonium chloride in 20 c.c. of water. The resulting solution of levorotatory ammonium salt was observed as rapidly as possible in a 2-dm. tube, the temperature being 18.5°. The rate of diminution of the rotation was approximately twice as great as in the corresponding solution of sodium salt:

<i>t</i> (mins.).	Rotation.	$1/t \log a/(a-x).$
0.0	-1.72°	—
1.87	1.56	0.023
3.43	1.43	0.023
4.73	1.34	0.023
6.47	1.23	0.023
7.62	1.15	0.023
9.13	1.08	0.022
10.58	0.99	0.023
12.37	0.90	0.023
14.55	0.77	0.024
17.35	0.68	0.023
21.83	0.55	0.023
25.77	0.42	0.024
39.65	0.19	0.024

The constant 0.023 corresponds with a period of half-change of 13.1 minutes.

*Ammonium Salt in presence of Ammonium Hydroxide*.—These observations were made on a dextrorotatory solution prepared from 3.0 grams of morphine *d*-acid salt by digestion with 8.18 c.c. of a normal solution of ammonia, the morphine being removed in the manner described by filtration and extraction of the filtrate and washings with chloroform. The final volume was 14.5 c.c. The excess of ammonia present could not readily be determined, but the above quantities were adjusted so as to give an approximately *N*/10-solution. The concentration of the ammonium salt calculated from the quantity of morphine salt used was 0.47-*N*. The solution

was placed in a 2-dcm. tube, and kept between the observations in a thermostat at 20°:

$t$ (hours.).	Rotation.	$1/t \log a/(a-x)$ .
0.0	5.00°	—
1.66	4.36	0.0358
2.47	4.08	0.0358
3.57	3.73	0.0356
4.73	3.39	0.0357
5.83	3.12	0.0351
6.72	2.89	0.0354
8.30	2.64	0.0354

The mean value of the constant (0.0355) corresponds with a period of half-change of 8.48 hours. The rate of racemisation of the ammonium salt is therefore thirty-nine times less in the presence of this excess of ammonium hydroxide than under the conditions of the previously described experiment.

*Mutarotation of the Morphine d-Acid Salt in Aqueous Solution.*—

The morphine salt is readily soluble in cold water. If the aqueous solution is polarimetrically examined as soon as possible after its preparation, its levorotatory power is found to be quickly increasing. The change is, however, rapidly completed (practically), and after about seven minutes no further alteration in the rotation is to be detected. If the solution is now decomposed by the addition of a slight excess of ammonia and the morphine removed, the resulting ammonium salt is quite inactive. The mutarotation is therefore due to the racemisation of the acid component of the salt.

One gram of finely powdered morphine salt, giving ammonium salt of molecular rotation  $[M]_D 51.7^\circ$  ( $c = 0.844$ ) was added to 20 c.c. of water. As soon as most of the salt had dissolved, the solution was filtered, and its rotatory power observed in a 2-dcm. tube, the first observation being completed 1.75 minutes after first wetting the salt. The temperature was 26.5°:

$t$ (mins.).	Rotation.	$\Delta$ .	$\Delta$ (calc.).
0.0	-7.13°	0.51°	—
1.03	7.41	0.26	0.27°
1.91	7.50	0.17	0.15
2.72	7.58	0.09	0.09
4.77	7.66	0.01	0.02
6.70	7.66	0.01	0.01
12.13	7.67	0.00	0.00
$\infty$	7.67	—	—

Under  $\Delta$  are given the differences between the rotations observed, and the value finally attained. The numbers in the last column are calculated by means of the unimolecular formula,  $k$  being taken as 0.29, corresponding with a period of half-change of 1.04 minutes. They agree with the observed differences within the limits of experimental error.

*The Mutarotation of the Quinine Salts of the d- and l-Acids.*—The quinine salts are not sufficiently soluble in water to allow of satisfactory observations being made in that solvent, and although they possess a high solubility in alcohol, when brought into contact with it they form gummy masses, which pass comparatively slowly into solution. In the case of each salt, therefore, 0.8 gram was first finely ground up with 6 c.c. of ethyl acetate, and 12–14 c.c. of absolute alcohol then added to the mixture, when solution took place very rapidly. The solutions thus obtained were filtered and observed in a 2-dm. tube, the temperature being 20° in each case. The quinine *l*-acid salt used was a sample which gave sodium salt of molecular rotation  $[\text{M}]_D -67.3^\circ$  ( $c=0.731$ ), the quinine *d*-acid salt gave ammonium salt of molecular rotation  $[\text{M}]_D 40.4^\circ$  ( $c=0.947$ ).

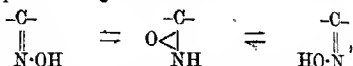
Quinine d-Oximinocyclohexane-4-carboxylate.				Quinine l-Oximinocyclohexane-4-carboxylate.			
<i>t</i> (mins.).	Rotation.	$\Delta$ .	$\Delta$ (calc.).	<i>t</i> (mins.).	Rotation.	$\Delta$ .	$\Delta$ (calc.).
0.0	-0.16°	0.44°	0.46°	0.0	-11.70°	0.89°	—
3.0	9.35	0.25	0.24	2.1	11.37	0.56	0.55
3.7	9.33	0.23	0.20	3.1	11.23	0.42	0.44
5.0	9.47	0.13	0.15	5.2	11.03	0.27	0.27
9.3	9.56	0.34	0.05	6.4	10.98	0.17	0.20
15.3	9.60	0.00	0.01	7.9	10.96	0.15	0.14
26.4	9.59	0.01	0.00	9.8	10.92	0.11	0.09
$\infty$	9.60	—	—	12.5	10.87	0.06	0.05
				21.7	10.82	0.01	0.01
				$\infty$	10.81	—	—

The levorotation was seen to increase in the case of the quinine *d*-acid salt and to diminish in that of the quinine *l*-acid salt, the rate of change agreeing (within the probable limits of error of the single rapidly made observations) with that calculated from the unimolecular formula when the velocity constant is taken as 0.1 in each case, corresponding with a period of half-change of three minutes.

The character of the differences among the velocity constants observed in these experiments might suggest that the rate of racemisation of the salts was connected with their degree of hydrolysis in the different solutions investigated—that the non-hydrolysed portion of the salt racemises very slowly, and that the observed loss of activity is mainly brought about through the rapidly racemising free acid present in larger or smaller proportion according to the degree of hydrolysis. It would appear, however, that this simple hypothesis is inadequate, for whereas the rates of racemisation in the aqueous solutions of the sodium and ammonium salts investigated were found to be approximately in the ratio of 2 to 1, the relative proportions of free acid present in the two solutions, calculated from the dissociation constants of water and



ammonia, were of the order of 100 to 1. Other factors must therefore probably be taken into account. For example, it is conceivable that the interconversion of the *d*- and *l*-modifications should take place through an iso-oximino-form:



and that the effects which acids and alkalis produce on the rate of racemisation are brought about through their influence on the relative proportion of the latter form present in the solutions.

The authors propose to extend this investigation to other compounds containing doubly-linked tervalent nitrogen. In conclusion, they desire to express their indebtedness to the Research Fund Committee of the Chemical Society for a grant by which the expenses of this work have been largely defrayed.

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### CC.—*Kinetics of the Reaction between Silver Salts and Aliphatic Iodides.*

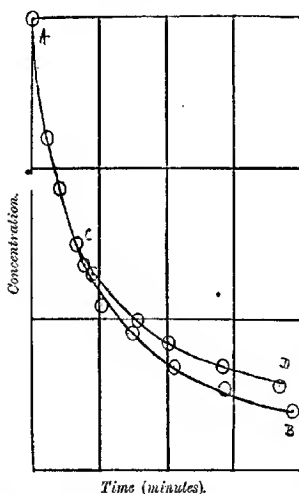
By FREDERICK GEORGE DONNAN and HAROLD EDWARD POTTS.

THE reaction between silver nitrate and alkyl iodides in alcoholic and aqueous-alcoholic solutions has been studied from a kinetic point of view by Burke and Donnan (Trans., 1904, 85, 555; *Zeitsch. physikal. Chem.*, 1909, 69, 148). The conclusion was drawn that the reaction is pseudo-bimolecular in type, and that the course of the reaction is affected by an accelerating influence due to some product. The following experiments have been carried out with the purpose of throwing further light on the mechanism of the reaction. They deal with the reaction between ethyl iodide and silver salts other than the nitrate, the reaction between ethyl iodide and silver nitrate in a non-hydroxylic solvent (acetonitrile), and the reaction between silver nitrate and aliphatic polyiodides (in alcoholic solution).

The diminution in the velocity-coefficient with decreasing initial concentration in the reaction between ethyl iodide and silver nitrate in alcohol led Burke and Donnan to the conclusion that the velocity of the reaction is accelerated by some product (although it was shown that this product could not be ethyl nitrate, ether, or nitric

acid). This fact is clearly shown by Fig. 1, in which the ordinates represent concentrations, and the abscissæ times. Curve  $AB$  represents the time-concentration curve for the reaction  $N/40\text{-AgNO}_3 + N/40\text{-C}_2\text{H}_5\text{I}$  in dry alcohol, whilst  $CD$  is the corresponding curve for the reaction  $N/80\text{-AgNO}_3 + N/80\text{-C}_2\text{H}_5\text{I}$  in the same solvent at the same temperature (Burke and Donnan, Trans. *loc. cit.*). In the figure, the time-zero for the second curve ( $CD$ ) has been shifted to the time-point (abscissa) when the primary reactants corresponding with the first curve ( $AB$ ) have fallen to a concentration of  $N/80$ . The non-coincidence of these curves and the greater steepness of  $AB$  show that the velocity of the reaction

FIG. 1.



is accelerated by some product. The reaction is therefore from a kinetic point of view a "disturbed" one, and the fair degree of constancy of the velocity-coefficient of the simple bimolecular equation in any particular experiment can only be explained as due to some compensating effect.

A special experiment made to test this conclusion showed that in the filtered reaction fluid resulting from a previous reaction, and containing no silver salt or alkyl iodide, the reaction proceeded (on addition of fresh portions of the reactants) more rapidly than in the pure solvent, the acceleration observed being in the ratio calculable from the results of Burke and Donnan.

In view of this disturbance, the constancy of the velocity-coefficient of the "bimolecular" equation in any given case does not prove that the reaction is really one of the second order. In the absence of the accelerating effect referred to, it is clear that the velocity-coefficient calculated from the simple bimolecular equation,  $-dc/dt = kc^2$ , would fall during the course of the reaction. This shows that the exponent of  $c$ , that is, the order of the reaction, must be higher than 2. In fact, although the Noyes-van't Hoff method is not strictly applicable to a case such as the present where the products exercise an accelerating influence, if we apply it to only a 10 per cent. change in the  $N/40$ - and  $N/80$ -reaction curves shown in Fig. 1, the value  $n=2.8$  is obtained for the exponent of  $c$ . It is possible that this result may be explained by considering the varying electrolytic dissociation of the silver nitrate, as described on p. 1889 (results with silver lactate in aqueous alcohol).

#### *Units and Method of Measurement.*

The "dry" alcohol used in the following experiments was prepared by long-continued boiling of the ordinary "absolute" alcohol with excess of freshly prepared calcium oxide.\* The alcohol so obtained was then freed from reducing substances by distillation from a small quantity of silver nitrate.

The reaction-velocities were all measured at 25°, and the amount of silver salt in solution estimated by titration with thiocyanate solution. The numbers given in the tables are expressed in terms of the following units. Unit of volume = 1 c.c.; unit of mass = fraction of a molecule contained in 1 c.c. of a  $N/100$ -solution. Thus, the concentration of a  $N/10$ -solution = 10. The velocity-coefficients calculated with these units are six times greater than those calculated with the units employed by Burke and Donnan in their first paper. The unit of time employed is one minute. The values of  $k$ , the velocity coefficient, have been calculated from the ordinary bimolecular equation except when otherwise stated.

The reaction fluids were previously warmed in separate vessels in the thermostat, and at a given time-point rapidly mixed. Definite equal volumes of the mixture were then quickly transferred by means of a previously warmed pipette into a series of small flasks placed in the thermostat.

#### *Experiments with Silver Lactate in Aqueous Alcohol.*

It has been shown in the case of silver nitrate that, although the velocity-coefficient of the bimolecular equation remains fairly constant in any given reaction, the velocity of the reaction is undoubtedly increased by some reaction product.

Experiments were therefore made with another silver salt in order to see if this peculiar behaviour could be associated with the presence of the  $\text{NO}_3$  group. Owing to the difficulty of getting silver salts sufficiently soluble in dry alcohol, the experiments were made with silver lactate in a composite solvent, obtained by mixing 40 volumes of water with 60 volumes of dry alcohol. It has been shown by Burke and Donnan that in a solvent of this composition the behaviour of silver nitrate and ethyl iodide resembles that in dry alcohol.

TABLE I.

Silver lactate,  $3N/200 \times 0.95$ ; ethyl iodide,  $3N/200$ .

$t$ .....	0	4.5	9.5	14.5	19.5	33	39.5	68.5
$c_{\text{Ag}}$ ..	1.43	1.285	1.16	1.07	1.00	0.835	0.785	0.615
$k$ .....	—	0.0161	0.0169	0.0152	0.0145	0.0141	0.0135	0.0128

It will be observed that the bimolecular velocity-coefficient falls steadily during the course of the reaction.

Determinations of the amount of free acid produced during the reaction were made, the results of which are shown in the following table.

TABLE II.

$t$	$c_{\text{ethyl}}$	$c_{\text{Ag}}$	Acid produced Silver used up $\times 100$ .
0	0.0	1.43	—
26	0.345	0.95	70
30	0.365	0.89	67
34	0.39	0.85	66
2 weeks	0.97	<0.01	70

The ratio of free acid produced to silver salt used up in the reaction remains constant. It is noteworthy that this ratio is practically the same as that observed by Burke and Donnan in the case of the reaction between silver nitrate and ethyl iodide in dry alcohol, although in this case the acid is different. The following two tables contain reaction-velocity measurements made with another sample of silver lactate at two different initial concentrations. The values of  $k$  are here calculated from point to point, and not from the beginning of the reaction to each time-point as in the previous table.

TABLE III.

Silver lactate,  $3N/100 \times 0.96$ ; ethyl iodide,  $3N/100$ .

$t$ .....	0	7	11	16	20	30	40
$c_{\text{Ag}}$ .....	2.89	1.76	1.525	1.31	1.21	1.00	0.88
$k$ .....	—	0.0302	0.0209	0.0200	0.0147	0.0157	0.0121

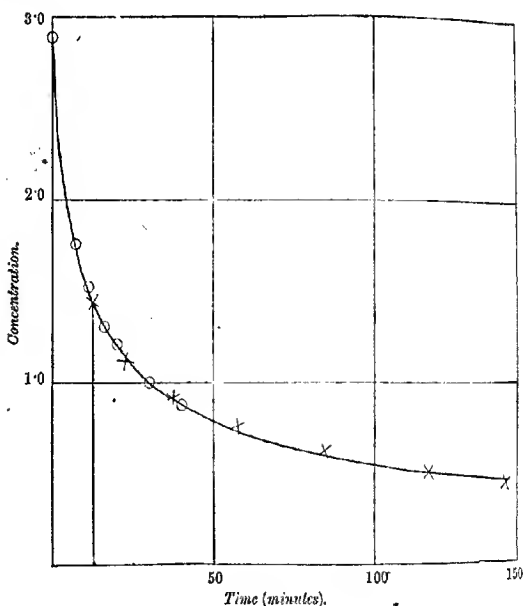
TABLE IV.

Silver lactate,  $3N/200 \times 0.96$ ; ethyl iodide,  $3N/200$ .

$t$ .....	0	10	25	45	72	105	133	180
$c_{Ag}$ ...	1.445	1.118	0.917	0.765	0.627	0.508	0.442	0.39
$k$ .....	—	0.0205	0.0120	0.0100	0.0099	0.0103	0.0095	0.0098

If these two sets of times and concentrations are plotted, and the time-zero for the  $3N/200$ -reaction made to coincide with the time-

FIG. 2.



point where the primary reactants of the  $3N/100$ -reaction have fallen to  $3N/200$ , as shown in Fig. 2, it will be seen that the two sets of points lie on the same continuous curve. This is in striking contrast to the case previously discussed (reaction between silver nitrate and ethyl iodide), and shows that in the present case the previously observed acceleration due to the products is absent.

It seems to be pretty certain therefore that in the case of silver nitrate the apparent constancy of the bimolecular reaction-coefficient

is due to a compensating effect caused by the acceleration, referred to. This is well shown by the following table, which contains the results of some further measurements of this reaction in the composite solvent employed above.

TABLE V.

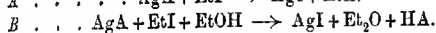
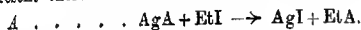
Silver nitrate, 3*N*/100; ethyl iodide, 3*N*/100.

<i>t</i> .....	0	6	19	49	90	124	164
<i>c</i> <sub>Ag</sub> .....	3.00	2.48	1.843	1.125	0.703	0.528	0.41
<i>k</i> .....	—	0.0117	0.0108	0.0116	0.0131	0.0136	0.0134

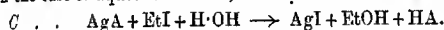
Here one observes a fair constancy of *k*, with, however, a tendency to increase towards the latter part of the reaction. A similar tendency is observable in some of the results previously given by Burke and Donnan (*loc. cit.*).

The practically constant ratio of lactic acid produced to silver lactate used up (66 to 70 per cent.) shows, as in the case of silver nitrate, that there must be at least two simultaneous reactions, in one of which the free acid is formed (Wegscheider's criterion).

Denoting the negative ion of the silver salt by A, we may represent these two reactions thus:



In the case of aqueous solvents, there will also occur the reaction:



In the case of alcoholic or aqueous-alcoholic solvents, the reaction *B* (or *B*+*C*) is the main one, as only about 30 per cent. of the "theoretical" amount of the ester EtA is produced.

In order to explain this "abnormal" production of acid, Wegscheider and Fränkel (*Sitzungsber. Wien. Akad.*, 1907, 116, Abt. IIb) have proposed the following hypothesis. They suppose that the essential cause of the reaction is the affinity of the silver and halogen atoms, and that this leads to a series of not sharply distinguishable intermediate stages in which there occurs a spatial approximation of the silver and halogen atoms. These may be roughly formulated as follows:



As a result of this, the "affinity" between  $C_2H_5$  and I on the one hand, and Ag and  $NO_3$  on the other is weakened, so that the above system may rearrange itself into the definite end-products AgI and  $C_2H_5 \cdot NO_3$ , or may react with a molecule of the solvent to give (in the case of ethyl alcohol) the end-products AgI,  $(C_2H_5)_2O$ , and  $HNO_3$ .

It would seem difficult to distinguish between this hypothesis and

what is usually understood by the assumption that a transient intermediate compound between the silver salt and the alkyl iodide is the first stage in the reaction. Moreover, Wegscheider's hypothesis does not lend itself to analytical treatment in the present condition of chemical science, so that it is impossible to apply to it any exact experimental test. We shall content ourselves therefore with examining the consequences of more definite hypotheses. In the first place, let us suppose that the velocity of the reaction is controlled by a direct interaction between one molecule of undissociated silver salt and one molecule of alkyl iodide. Considering only equivalent concentrations, and calling  $a$  the degree of dissociation of the silver salt, this leads to the equation:

$$-dc/dt = k(1-a)c^2.$$

As  $a$  will increase, and therefore  $1-a$  decrease, with the progress of the reaction, the coefficient  $k(1-a)$  of the simple bimolecular equation will diminish as the reaction progresses. This is exactly what the experimental results show in the case where the reaction is not disturbed by the products. Let us now make the further assumption that the simple law of mass-action holds for the equilibrium between the undissociated silver salt and its ions. This leads to the equation  $K(1-a) = a^2c$ , which, combined with the previous one, gives:

$$-dc/dt = k'a^2c^3.$$

Now, as  $a$  increases with the dilution, we should expect the coefficient  $k'a^2$  of the "termolecular" equation to increase with the progress of the reaction, but as, at the dilutions employed,  $a$  will not differ very far from unity, it is obvious that the increase of  $k'a^2$  will be considerably smaller than the decrease of  $k(1-a)$ .

The following table contains the values of  $k_3$  corresponding to the equation  $-dc/dt = k_3c^3$ , as calculated from the curve given in Fig. 2.

The values of  $k_3$  are calculated from point to point.

TABLE VI.

$t$ .....	0	4.2	11.1	30.1	48.5	84.7	119.0
$c$ .....	2.69	2.0	1.5	1.0	0.8	0.6	0.5
$k_3$ .....	—	0.0298	0.0281	0.0292	0.0306	0.0336	0.0356

The coefficient of the simple bimolecular equation falls from 0.030 to 0.010 over the same range of concentration. The constancy of  $k_3$  is surprising, and, indeed, even greater than could have been expected on the above hypothesis. This will be made clear by the following table:

$a$ .....	0.7	0.8	0.9
$a^2$ .....	0.49	0.64	0.81
$1-a$ .....	0.30	0.20	0.10

This table shows that if  $(1-a)$  falls in the ratio of 3 to 1,  $a^2$  will increase by more than 50 per cent. Now, whilst the fall of the bimolecular velocity-coefficient is in reality in the ratio 3:1, the corresponding increase in the termolecular velocity-coefficient is only about 20 per cent. Too much stress need not be laid on this discrepancy, as the assumption that the simple law of mass-action holds for the electrolytic dissociation of the silver salt may be only a very rough approximation.

It is necessary also to remark here that if the simple law of mass-action be assumed, the equation  $-dc/dt = k'a^2c^3$  can be equally well reconciled with the view that only the ions  $\text{Ag}'$  and  $\text{NO}_3'$  react with the alkyl iodide. The results appear to show, however, that the reaction velocities due to undissociated silver nitrate on the one hand, and the ions  $\text{Ag}'$  and  $\text{NO}_3'$  on the other, must be very different, so that the main effect must be due to either one or the other. Experiments carried out in alcohol as solvent have shown (Burke and Donnan, *Zeitsch. physikal. Chem., loc. cit.*) that highly dissociated nitrates, such as ammonium nitrate, considerably increase the velocity of the reaction between silver nitrate and ethyl iodide. This seems to indicate that it is the undissociated silver nitrate molecules which are effective (at all events, in alcoholic solution).

Concerning the question of the formation of an intermediate compound, the experimental results are not decisive. If, as seems possible from the above, it is the undissociated silver salt which reacts, then it is a plausible hypothesis to assume that the velocity of the whole reaction is determined by the rate of formation of an intermediate compound between the silver salt and the alkyl iodide, this intermediate compound then rapidly changing to alkyl ester and silver iodide on the one hand, and, on the other, reacting with a molecule of solvent to form silver iodide, free acid, and an ether (or alcohol). There is, however, no experimental evidence which would enable one to test this hypothesis.

#### *Experiments with Silver Nitrate in Acetonitrile.*

The foregoing experiments, together with those of Nef (*Annalen*, 1899, 309, 126), Burke and Donnan (*loc. cit.*), and Wegscheider and Fränkel (*loc. cit.*), have shown that when a silver salt reacts with an alkyl iodide in a solvent which contains the hydroxyl group, free acid is one of the main products. It was decided therefore to carry out some experiments in a non-hydroxylic solvent in order to examine the kinetics of the reaction when no free acid can be formed. As a few preliminary experiments showed that the reaction between silver nitrate and ethyl iodide proceeds with con-





TABLE VIII.

Silver nitrate,  $N/20$ ; ethyl iodide,  $N/20$ .

$t$ .....	0	15.5	41	84	139	196	244
$\text{CAG}$ .....	5.00	4.68	4.09	3.32	2.87	2.47	2.20
$k$ .....	—	0.00090	0.00107	0.00120	0.00107	0.00105	0.00105

 $k$  (mean) = 0.00105.

TABLE IX.

Silver nitrate,  $N/40$ ; ethyl iodide,  $N/40$ .

.....	0	91	248	349
$\text{Ag}$ .....	2.50	2.11	1.66	1.47
$k$ .....	—	0.00081	0.00081	0.00081

 $k$  (mean) = 0.00081.

In these experiments the reaction-liquid at the end of the reaction was found to contain a small quantity of acid, but this was traced to the solvent, which was found to contain a small quantity of phosphoric acid sufficient to explain the acidity of the reaction-fluid. To obviate this, the acetonitrile, which had been previously dried by phosphoric oxide as described, was treated with freshly ignited lime and redistilled. The following experiment was carried out with the now neutral distillate:

TABLE X.

Silver nitrate,  $N/20$ ; ethyl iodide,  $N/20$ .

$t$ .....	0	98	130	157	166
$\text{CAG}$ .....	5.00	3.33	2.95	2.73	2.73
$k$ .....	—	0.00102	0.00106	0.00106	0.00100

 $k$  (mean) = 0.00104.

This value of  $k$  agrees very well with that previously found. It was noticed, however, that at the end of the experiment the reaction-fluid contained about the same (small) quantity of free acid as in the previous experiments. Probably the acetonitrile, after treatment with phosphoric oxide, contained a little ethyl phosphate (due to traces of alcohol), and this on distillation from lime regenerated the alcohol, which afterwards reacted to form free acid.

The above experiments prove that whilst the reaction proceeds normally (that is, without production of free acid) in acetonitrile as solvent, the reaction-kinetics closely resemble those obtained with alcohol as solvent. The simple bimolecular velocity-equation holds good for each experiment (although in the case of the  $N/10$ -reaction there is a decided drop), but the velocity-coefficient varies with the initial concentrations of the reactants. It is clear that the peculiar

kinetic behaviour observed in hydroxylic solvents has nothing to do with the acid formation. As explained previously, this behaviour is probably to be accounted for by the varying dissociation of the silver salt, and, in the case of the nitrate, by the formation of some product which acts as an accelerator.

If time-concentration curves for the experiments with various initial concentrations be plotted as described on p. 1883, it will be found that in the case of acetonitrile as solvent the various curves so obtained cannot be made to superimpose, although the divergence is not nearly so marked as in the case of alcohol as solvent. This would seem to show that the accelerating effect referred to above is much smaller in the experiments with silver nitrate in acetonitrile.

*Experiments with Iodoform in Alcoholic Solution.*

\* Preliminary experiments showed that in dry ethyl alcohol at 25°, silver nitrate and iodoform (both  $N/30$ ) react with convenient speed, the reaction occurring in the stoichiometric ratio  $3\text{AgNO}_3 : \text{CHI}_3$ , and the precipitate produced being silver iodide. During the reaction free nitric acid is produced, and this slowly liberates iodine from iodoform, but if the experiment does not last more than a few hours, this secondary reaction may be neglected. The following tables contain the results of the velocity measurements ( $k$  = coefficient of simple bimolecular equation):

TABLE XI.

$N/25\text{-AgNO}_3; N/25\text{-(CHI}_3/3\text{)}.$

$t$ .....	0	80	45	60	120	210
$c_{\text{Ag}}$ ...	3.765	3.255	3.055	2.825	2.34	1.74
$k$ .....	—	0.00136	0.00136	0.00146	0.00135	0.00147

Mean = 0.00140.

TABLE XII.

$N/30\text{-AgNO}_3; N/30\text{-(CHI}_3/3\text{)} \text{ (temp. = } 25.2^\circ\text{)}.$

$t$ .....	0	52	70	82	92	116	155	173
$c_{\text{Ag}}$ ...	3.185	2.595	2.55	2.47	2.445	2.29	2.06	1.955
$k$ .....	—	0.00136	0.00111	0.00111	0.00103	0.00109	0.00110	0.00119

Mean = 0.00113.

TABLE XIII.

$N/40\text{-AgNO}_3; N/40\text{-(CHI}_3/3\text{)}.$

$t$ .....	0	52	71	94	148	167
$c_{\text{Ag}}$ ...	2.45	2.265	2.175	2.13	1.945	1.87
$k$ .....	—	0.00066	0.00073	0.00095	0.00072	0.00076

Mean = 0.00070.

TABLE XIV.

 $N/30\text{-AgNO}_3; N/40\text{-(CHI}_3/3\text{)}.$ 

$t$ .....	0	19.25	42.5	85	98	210	232	303
$c_{\text{Ag}}$ ..	3.33	3.185	3.015	2.725	2.675	2.185	2.035	2.015
$k$ .....	—	0.00090	0.00098	0.00107	0.00103	0.00110	0.00122	0.00097

Mean = 0.00104.

TABLE XV.

 $N/52\text{-AgNO}_3; N/40\text{-(CHI}_3/3\text{)}.$ 

$t$ .....	0	28	109	142	180	231	257
$c_{\text{Ag}}$ .....	1.93	1.835	1.645	1.54	1.495	1.375	1.345
$k$ .....	—	0.00062	0.00064	0.00070	0.00063	0.00071	0.00063

Mean = 0.00065.

An experiment was tried with a solution of iodoform in alcohol which had been preserved in the dark for eleven days. This solution reacted with silver nitrate with the same speed as a fresh solution.

The following table summarises the results obtained with iodoform:

TABLE XVI.

Initial concentration.	Value of $k \times 10^5$ .
$N/25$ .....	140
$N/30$ .....	113
$N/40$ .....	70
$N/30\text{-AgNO}_3; N/40\text{-(CHI}_3/3\text{)}.$	104
$N/40\text{-AgNO}_3; N/52\text{-(CHI}_3/3\text{)}.$	65

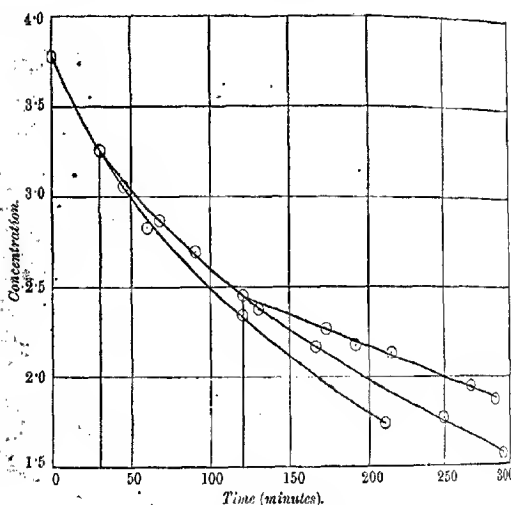
It will be observed that the behaviour of iodoform closely resembles that of an alkyl moniodide. The reaction is pseudo-bimolecular in type, the velocity-coefficient increasing rapidly with increasing initial concentrations of the reactants, and being mainly dependent on the initial concentration of the silver nitrate. If time-concentration curves be plotted, the curves representing reactions starting at different initial concentrations cannot be superimposed, the reaction which starts at a lower initial concentration always proceeding markedly slower than a reaction which has reached the same concentration of the reactants from a higher initial concentration. As shown in Fig. 4, this divergence is greater than in the case of the reaction between silver nitrate and ethyl iodide in alcohol as solvent.

The constancy of the bimolecular velocity-coefficient in spite of such a great acceleration due to the products proves that in the absence of this disturbing effect the order of the reaction would be much higher than 2. Indeed, an application of the Noyes-van't Hoff method to the initial portions (10 per cent. change) of the various reaction-curves plotted above yields, for the order of the reaction,

numbers the mean of which is about 3.8. It is probable therefore that the real order of the reaction is between 3 and 4, and nearer 4 than 3. With the data at hand, it is not possible to go further than this. In particular, it is not possible to decide whether the reaction proceeds in a series of successive stages, though the somewhat analogous case of the alkali hydrolysis of the triglycerides would render this view probable.

As in the case of the alkyl iodides, the reaction proceeds with formation of free acid. For the reaction starting at  $N/30$ .

FIG. 4.



equivalent concentrations of silver nitrate and iodoform, the free nitric acid found at the completion of the reaction was equivalent to 85 per cent. of the original silver nitrate. This is a higher amount than that observed in the case of ethyl iodide.

The following experiment is a good example of a "rapid" reaction, in which one of the reactants is a carbon compound. If a small quantity of finely powdered silver nitrate be cautiously mixed with the equivalent amount of solid iodoform, a scratch or light blow is sufficient to set up a violent reaction, in which clouds of iodine vapour and oxides of nitrogen are evolved.

*Experiments with Methylene Iodide and Carbon Tetraiodide in Alcoholic Solution.*

The experiments recorded in the previous section show that iodoform reacts with silver nitrate in alcoholic solution at 25° about eight times more slowly than methyl iodide. A few experiments carried out with methylene iodide and silver nitrate in alcoholic solution showed that the velocity-coefficient is about one hundred times smaller than the corresponding coefficient for iodoform. In point of reactivity with silver nitrate, methylene iodide does not therefore occupy a position intermediate between methyl iodide and iodoform, but is characterised by a very great sluggishness.

Carbon tetraiodide was prepared by a modification of Gustavson's method, but it was found impossible to carry out any satisfactory measurements of its velocity of reaction with silver nitrate, as in alcoholic solution the tetraiodide loses iodine with comparative rapidity. Some special experiments on this point showed that in a solution containing 0.1 gram of tetraiodide in 20 c.c. of alcohol, 95 per cent. of the iodine of the tetraiodide is present as free iodine after sixteen hours.

On adding an alcoholic solution of silver nitrate to an alcoholic solution of carbon tetraiodide there is an immediate diminution in the amount of dissolved silver salt, due to interaction with the free iodine. After this, the concentration of the silver salt diminishes very slowly, so that the carbon tetraiodide itself does not react at all rapidly with silver nitrate in alcoholic solution.

In conclusion, the authors desire to express their best thanks to the Research Fund Committee of the Chemical Society for a grant which helped to defray the expenses of this investigation.

*Note.*—Since the completion of the above work, a paper has appeared by G. Senter (Trans., 1910, 97, 346), in which this author finds that in the reaction between silver nitrate and methyl iodide in alcoholic solution, precipitated (or colloidal) silver iodide exerts a slight accelerating effect on the velocity of the reaction. It may be possible therefore that this is the product of the reaction which produces the accelerating effect discussed in the foregoing paper. It is somewhat difficult, however, to reconcile this view with the apparent absence of the accelerating action in the reaction between silver lactate and ethyl iodide in aqueous-alcoholic solution. The matter requires further investigation before this point can be definitely settled.

CCI.—Changes in<sup>\*</sup> Volume in the Formation of Dilute Solutions. Part II. Relationship between Change in Volume and Constitution.

By HARRY MEDFORTH DAWSON.

IN Part I of this work (this vol., p. 1041) an account was given of the volume changes which occur in the formation of dilute solutions of iodine and naphthalene. From the fact that the sequence of the solvents, when arranged according to the magnitude of the volume changes, is quite different for the two dissolved substances, the conclusion was drawn that these changes in volume cannot, in general, be interpreted in terms of any property or properties of the pure solvents. This was shown to be the case whether it is assumed that the observed volume change is entirely due to a change in the volume of the dissolved substance, or whether the change is debited entirely to the solvent.

There can be no doubt that neither of these limiting views is correct, and according to Tammann (*Zeitsch. physikal. Chem.*, 1896, **21**, 529), the volume change  $\Delta v$  occurring in the formation of a solution must in general be represented by an equation of the form:

$$\Delta v = \Delta\phi_1 + \Delta\phi_2 + \Sigma\Delta\phi \dots (1).$$

In this equation  $\Delta\phi_1$  and  $\Delta\phi_2$  represent respectively the alterations in volume experienced by the solute and the solvent when the pressures acting on these are changed from the values representing the internal pressures of the pure substances to the common internal pressure of the solution. The term  $\Sigma\Delta\phi$  represents the further change in volume which is supposed to take place when the solvent and solute are then mixed together without any alteration in the value of the pressure to which the components of the system are subjected.

In justification of the term  $\Sigma\Delta\phi$ , Tammann cites the experimental measurements of Braun (*Ann. Physik*, 1888, [iii], **34**, 943), according to which the mixing of gases, even at atmospheric pressure, is accompanied by appreciable volume changes. The inference drawn by Tammann from these observations does not appear, however, to be very conclusive. In the first place, it should be noticed that in Braun's experiments, the different gases were allowed to mix without change in the manometrically measured pressure. For one and the same external pressure, the gases are, however, subjected to different internal pressures or total pressures, and this is more particularly so in the case of the more easily condensible gases; such as sulphur dioxide and carbon dioxide, which,

when mixed with equal volumes of hydrogen or nitrogen, were found to give rise to relatively large changes of volume at atmospheric pressure. Furthermore, the internal pressure of the mixed gases will, in general, be different from the internal pressures of the unmixed gases, although the manometrically measured pressure retains the same value. Some idea of the magnitude of the volume changes, which may result from the operation of these internal pressure differences, is obtained if we consider the variation of the product  $pv$  at low pressures. According to measurements of Fuchs (Castell-Evans, *Physico-chemical Tables*, p. 450), the value of  $pv$  changes in the ratio 1:1.0251 for sulphur dioxide, 1:1.0063 for carbon dioxide, and 1:0.9988 for air when the pressure is reduced from 1000 to 250 mm. of mercury.

From the above considerations, it would appear that the deviations from the additive law of gas volumes observed by Braun are not directly applicable to the process of the mixing of liquids (or gases) under the conditions stipulated by Tammann.

We may now consider the admixture of two different liquids  $A_1$  and  $A_2$  a little more closely from the point of view of internal pressure, or rather from that of the molecular forces of attraction which give rise to this pressure. If the specific molecular attraction of the pure liquids is denoted by  $a_1$  and  $a_2$ , and the corresponding attraction between the molecules of  $A_1$  and  $A_2$  by  $a_{1,2}$ , and if the molecular volumes of the unmixed liquids are  $v_1$  and  $v_2$  and the volume of the mixture is  $v_{1,2}$ , then the internal pressures of  $A_1$ ,  $A_2$ , and  $(A_1 + A_2)$  are given by  $a_1/v_1^2$ ,  $a_2/v_2^2$ , and

$$(a_1/v_{1,2}^2 + a_2/v_{1,2}^2 + 2a_{1,2}/v_{1,2}^2)$$

respectively. In the ideal process of mixing, from the consideration of which equation (1) is derived, the two internal pressures  $a_1/v_1^2$  and  $a_2/v_2^2$  are supposed to be reduced to the common value  $(a_1 + a_2 + 2a_{1,2})/v_{1,2}^2$  before the actual mixing is carried out. If these conditions are fulfilled, it is difficult to see on what grounds a change in volume corresponding with  $\Sigma \Delta \phi$  is to be anticipated. In the author's opinion the conditions of the process are such as to preclude the possibility of such a volume change, and equation (1) reduces therefore to the simpler form:

$$\Delta v = \Delta \phi_1 + \Delta \phi_2 \quad \dots \dots \dots (2).$$

In reference to the validity of this equation as an expression of the volume change which occurs in the mixing of two liquids, it should be noted that it is tacitly assumed that the mixing process is not accompanied by any change in the molecular complexity of either of the two liquids, that is to say, by association or dissociation phenomena, nor yet by any change in the nature of chemical combination between the two sets of molecules. Pairs of substances



which satisfy these conditions may for convenience be referred to as "normal" substances, and the solutions obtained by mixing them as "normal" solutions.

As a consequence of the elimination of the term  $\Sigma \Delta \phi$  from equation (1), the expression for the change in volume which occurs in the formation of a solution is greatly simplified. If the specific volumes of the two components (solute and solvent) in the pure liquid condition are denoted by  $\phi_1^l$  and  $\phi_2^l$ , and the true volumes of these components in the solution containing  $x$  parts of  $A_1$  and  $(1-x)$  parts of  $A_2$  are represented by  $\phi_1^s$  and  $\phi_2^s$ , the change of volume in the formation of unit quantity of solution may be written:

$$\Delta v = x(\phi_1^l - \phi_1^s) + (1-x)(\phi_2^l - \phi_2^s) \quad \dots \quad (3).$$

If  $P_1$  and  $P_2$  are the internal pressures of the pure liquids,  $P_3$  that of the solution, and if  $\beta_1$  is the mean compressibility of  $A_1$  (referred to unit quantity) between the pressure limits  $P_1$  and  $P_3$ , and  $\beta_2$  is the corresponding value of the compressibility of  $A_2$  between  $P_2$  and  $P_3$ , the above equation may be written in the form:

$$\Delta v = x\beta_1(P_1 - P_3) + (1-x)\beta_2(P_2 - P_3) \quad \dots \quad (4).$$

According to this equation, the change in volume is dependent on the proportions of the two substances in the solution and on their compressibilities between certain limits of pressure. Of these limiting pressures,  $P_3$  is common to the two substances, and is a function of  $x$ , the value of which determines the composition of the solution. According to results obtained by von Biron (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 188) for pairs of liquids which appear to conform to the above definition of "normal" pairs,  $P_3$  is a linear function of  $x$ , and its connexion with the internal pressures  $P_1$  and  $P_2$  of the pure liquids is given by  $P_3 = xP_1 + (1-x)P_2$ . If this result is accepted as a first approximation, substitution for  $P_3$  in equation (4) leads to:

$$\Delta v = x(1-x)(P_1 - P_2)(\beta_1 - \beta_2) \quad \dots \quad (5).$$

In the case of a dilute solution in which one of the components (the solvent) is present in large excess,  $x$  may be neglected in comparison with unity, and equation (5) may then be written in the form:

$$\Delta v/x = (P_1 - P_2)(\beta_1 - \beta_2) \quad \dots \quad (6),$$

in which  $\Delta v/x$  is the change in volume referred to unit quantity of the solute.

According to this, the volume change which accompanies the formation of dilute solutions of one and the same substance ( $P_1 = \text{constant}$ ) in different solvents is dependent on the internal pressure  $P_2$  of the solvent and on the compressibilities  $\beta_1$  and  $\beta_2$  of

the solute and solvent respectively. The compressibilities are, of course, dependent on the pressure limits which are involved in a particular case, and in the absence of a sufficiency of data connecting pressure and compressibility it is not possible to subject equation (6) to a rigorous experimental examination. We may, however, enquire to what extent the relative magnitudes of the changes of volume observed in the formation of the dilute solutions investigated in the first part of this paper are in agreement with the requirements of this equation, according to which the change in volume is influenced by two independent factors, one of which may be referred to as the internal pressure factor, and the other as the compressibility factor. If now we compare solvents of approximately equal internal pressures, but considerably different compressibilities, then according to equation (6) we may expect to find a connexion between the relative volume changes and the compressibilities of the solvents. On the other hand, if solvents are compared which have approximately equal compressibilities and different internal pressures, it is to be anticipated that the volume changes will be related to the internal pressure values.

Such relationship may not, however, be apparent unless the conditions stipulated in connexion with equation (2) are fulfilled. The solutions must be "normal" in the sense already defined; that is to say, the formation of the solutions must not be accompanied by changes in the degree of complexity of the solute or solvent, and the solute must not enter into chemical combination with the solvent.

In the case of dilute solutions of iodine which will be specially discussed in this paper, molecular-weight determinations have shown that the first condition in regard to the solute is fulfilled quite generally. Whatever the nature of the solvent, dissolved iodine appears to be present in the form of diatomic molecules. Experiment furnishes no evidence in respect of the constancy of the degree of complexity of the solvent, but for dilute solutions it is safe to assume that this condition is generally satisfied by the different solvents. It is, however, an entirely different matter in regard to the absence of chemical combination.

Recent work relating to the cause of the differences in colour of iodine solutions appears to point to the conclusion that these differences are due to variations in the extent to which iodine is combined with the solvent. From these investigations, in reference to which attention may be called to a paper by Waentig (*Zeitsch. physikal. Chem.*, 1909, 68, 513), it is probable that violet-coloured solutions of iodine are those which approximate more closely to what have been termed "normal" solutions than do the red and

brown solutions. As the ability to transmit the more refrangible visible rays diminishes, the deviation from this "normal" type increases, and an increasing proportion of the dissolved iodine is chemically combined with the solvent.

The extent to which the formation of solvates may modify the volume changes which occur in the formation of solutions cannot be estimated in any particular case. It is very probable, however, that these complex molecules are formed with a diminution in volume the magnitude of which will depend on the specific nature of the solvent. This view is supported by the results of experiments in which iodine was dissolved in solvents containing soluble polyiodides. At the same time, some idea is obtained of the extent to which the chemical combination of the dissolved iodine may influence the observed volume changes.

Experiments were made with solutions of potassium iodide and iodine in nitrobenzene and in ethyl acetate. In these solutions the added iodine combines to a large extent with the dissolved substance or substances already present to form a higher polyiodide or polyiodides, and the difference between the "solution volumes" represents therefore the "molecular solution volume" of combined iodine as distinguished from that of free iodine, the corresponding values for which are appended for comparison in the table:

	Nitro- benzene.		Ethyl acetate.
"Solution volume" of KI + 3I.....	198.3 c.c.	KI + 4I.....	147.3 c.c.
"                  " KI + 5I ....	133.1 "	KI + 6I.....	210.5 "
"Molar sol. vol." of combined iodine	65.2 "	combined iodine.	63.2 "
"                  " free iodine .....	67.2 "	free iodine .....	64.5 "

Since the polyiodide solutions in the case of both solvents are good conductors, and therefore ionised to a considerable extent, and since changes in the degree of ionisation are accompanied by appreciable changes in volume (compare Walden, *Zeitsch. physikal. Chem.* 1907, 60, 87), conductivity measurements were made before and after the addition of iodine to ensure that no changes in volume due to this factor were involved. From the values of the "molecular solution volume" of the free and combined iodine, it is evident that the combination of the iodine is accompanied by a contraction of 2 c.c. per gram-molecule in nitrobenzene solution, and of 1.3 c.c. in the solution in ethyl acetate. Volume changes of this order of magnitude may therefore be expected in the formation of so-called solvates.

If the change in volume resulting from the chemical combination is relatively small, the effect of the solvate formation may not be sufficient to modify appreciably the influence of those factors which otherwise determine the connexion between the total volume change

and the nature of the solvent. On the other hand, if the change in volume due to solvate formation is relatively large, the influence of the internal pressure and the compressibility of the solvent on the observed change in volume may be completely overshadowed.

From equation (6) and the above considerations relating to solvate formation, it follows that, in general, the volume changes which occur when the same quantity of iodine is dissolved in different solvents to form dilute solutions are dependent on (1) the internal pressure of the solvent, (2) the compressibility of the solvent, and (3) the contraction which accompanies the chemical combination of a smaller or larger proportion of the iodine with the solvent.

Whatever the nature of the dissolved substance, these are the determining factors, and the only reason for the selection of iodine for consideration is the fact that more evidence in regard to its molecular condition in solution in different types of solvents has been obtained than in the case of any other single substance. The advantages attaching to the examination of a coloured substance, such as iodine, which is characterised by specific activity towards visible light rays, are not inconsiderable from the point of view of the general theory of solutions. Other specific properties, such as optical rotatory power, are of still greater value in connexion with quantitative measurements, and the importance of optical activity on the part of one of the components of a solution in connexion with the investigation of the nature of solutions has been rightly emphasised by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 590, 641, 685).

From the experimental data for solutions of iodine and naphthalene recorded in Part I. (*loc. cit.*), the conclusion was drawn that the changes in volume associated with different solvents cannot in general be accounted for by reference to the internal pressures or other properties of the solvents. This conclusion is consistent with the result which is now obtained as a consequence of a closer examination of the factors which are operative in determining these volume changes. In view of the fact that the volume change is, in general, determined by three independent factors, it is not possible to subject the experimental results to any very detailed analyses. Certain relationships having an obvious connexion with the view developed in this paper may, however, be referred to.

When the fifteen solvents investigated are arranged according to the magnitude of the change in volume which occurs when iodine is dissolved in them, we obtain a series in which nitrobenzene is the first member, and ethyl ether the last. Per gram-molecule of iodine, the formation of a solution in nitrobenzene is accompanied

by an expansion of 8.7 c.c., and in ethyl ether by a contraction of 8.0 c.c.\* Of all the solvents examined, nitrobenzene is the least compressible, and ethyl ether is by far the most compressible, and since the internal pressures of the two liquids are not very different, the observed volume changes are obviously in accordance with what would be anticipated from equation (6). With naphthalene as dissolved substance, the relative volume changes in the case of these two solvents are quite similar, in that nitrobenzene, as the second member of the series of fifteen solvents, shows the next largest expansion, whilst ethyl ether gives rise to by far the largest contraction.

Carbon tetrachloride and carbon disulphide are two other solvents which may be compared. Both yield violet solutions, and the dissolved iodine is therefore probably present, for the most part, in the free condition; their compressibilities also appear to be approximately equal. In these circumstances a connexion between the volume changes and the internal pressures of the solvents may be expected. According to Walden and Traube, the internal pressure of carbon disulphide is about 50 per cent. greater than that of carbon tetrachloride, and in agreement with this it is found that the solution of one gram-molecule of iodine in carbon tetrachloride is accompanied by an expansion of 7.3 c.c., whereas the corresponding expansion for the solution in carbon disulphide is only 2.6 c.c. When the volume changes associated with the formation of solutions of naphthalene in these two solvents are compared, the relative positions are, however, reversed. For a gram-molecule of naphthalene, there is a contraction of 0.75 c.c. in carbon tetrachloride, and an expansion of 1.35 c.c. in carbon disulphide. In the case of naphthalene there is no evidence of the molecular condition of the dissolved substance apart from its degree of complexity, and the relative volume changes lead to the supposition that the naphthalene enters into combination with carbon tetrachloride to form addition compounds to a greater extent than it does in the case of carbon disulphide.

In reference to the view that brown solutions of iodine contain a considerable proportion of the iodine in combination with the solvent, the fact may be mentioned that all solutions which contain combined iodine in the form of polyiodides of the alkali and alkaline earth metals and of hydrogen appear to have a brown colour. In certain cases, as, for example, the brown solution in pyridine, direct evidence of combination of iodine with the solvent has been obtained by the isolation of a crystalline compound (Waentig, *loc. cit.*). In others, the brown colour is probably due in a large measure to

\* These changes in volume refer to the liquid solute.

iodine compounds which are formed as a result of double decomposition. Acetone, which has been frequently used as a solvent for iodine in investigations relating to the cause of the differences in colour exhibited by iodine solutions, belongs to this class.

It has been shown (Dawson and Leslie, *Trans.*, 1909, **95**, 1860) that iodine reacts rapidly with acetone, forming hydrogen iodide and acetone, and that a condition of equilibrium is established as a consequence of the reversibility of the reaction. In the case of a solution, prepared by dissolving one gram-molecule of iodine in 100 gram-molecules of acetone, about 45 per cent. of the iodine is converted into hydrogen iodide. In the resulting solution, the iodine, which has not been acted on by the acetone, is largely combined with the hydrogen iodide in the form of a polyiodide, and, in all probability, the colour and the absorption spectrum of this solution correspond with that of iodine, which is thus combined with one of the products resulting from the interaction of the solute and the solvent. Other ketones react similarly with iodine, and it is not unlikely that the colour of solutions of iodine in other solvents may be in part due to the same cause.

These facts add weight to the conclusion that solutions of iodine do not, in general, belong to the type of "normal" solutions as defined in this paper, and on this account the absence of any general connexion between the measured changes in volume and the formation of these solutions and the internal pressures and compressibilities of the solvents is not surprising. It may be that solutions of naphthalene approximate more closely to this type, but, in any case, the observed lack of parallelism between the volume changes for these two substances in the same series of solvents is consistent with the view that the dissolved substances combine to an appreciable extent with the various solvents.

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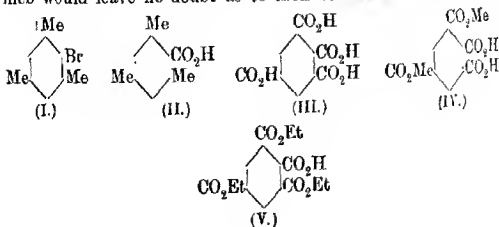
CCII.—*The Constitution of the Benzenetetracarboxylic Acids.*

By HANNAH BAMFORD and JOHN LIONEL SIMONSEN.

DURING the course of an investigation which is described in the succeeding paper (p. 1910), it became necessary definitely to determine the constitution of two of the benzenetetracarboxylic acids, namely, prehnitic and mellophanic acids. The three isomeric benzenetetracarboxylic acids were first obtained by Baeyer (*Annalen*, 1873, **166**, 325) during the course of his classical researches on mellitic acid. It is unnecessary here to enter into the reasoning by which he deduced the formulæ to be ascribed to these acids, and it will suffice to point out that whilst he proved conclusively (*loc. cit.*, p. 344) pyromellitic acid to be benzene-1:2:4:5-tetracarboxylic acid, he was unable to decide whether prehnitic acid was benzene-1:2:3:4- or -1:2:3:5-tetracarboxylic acid. He inclined to the latter view, however (*loc. cit.*, p. 344) because he found that this acid only yields a monoanhydride whilst if it had possessed four adjacent carboxyl groups it should give a dianhydride.

The question remained undecided until O. Jacobsen (*Ber.*, 1884, **17**, 2517) by the oxidation of *isodurene* obtained an acid which was shown by direct comparison to be identical with Baeyer's mellophanic acid. Now, since *isodurene* was obtained from bromomesitylene, it followed that mellophanic acid must be benzene-1:2:3:5-tetracarboxylic acid, and hence prehnitic acid would be the 1:2:3:4-isomeride. Further evidence in support of this view was obtained by Töhl (*Ber.*, 1888, **21**, 907), who oxidised prehnitic acid and isolated an acid which showed all the properties of prehnitic acid.

As the present authors had obtained results which seemed to throw some doubt on these experiments, it was decided to endeavour to devise methods for preparing prehnitic and mellophanic acids which would leave no doubt as to their constitution.



A ready means of carrying this out appeared to be to prepare mesitylenecarboxylic acid and to oxidise this to the corresponding tetrabasic acid.

Mesitylenecarboxylic acid (II) was found to be most conveniently obtained by the action of magnesium and carbon dioxide on bromomesitylene (I), and on oxidation with nitric acid under the conditions described in the experimental part of this paper (p. 1907), it was found to be converted quantitatively into benzene-1:2:3:5-tetracarboxylic acid (III).

The substance obtained in this way showed all the properties ascribed by Baeyer to the acid called by him prehnitic acid, and there can therefore be little doubt that this acid is really benzene-1:2:3:5-tetracarboxylic acid. This view also receives support from the following stereochemical considerations: (a) The acid yields only a monoanhydride (Baeyer, *loc. cit.*); (b) when esterified in the cold with methyl alcohol and hydrochloric acid it gives a dimethyl ester (compare Meyer and Sudborough, *Ber.*, 1894, 27, 1591), which probably has the constitution (IV); (c) when, however, the acid is esterified by means of alcohol and sulphuric acid by heating on the water-bath in the usual manner, it yields a triethyl ester which undoubtedly has the constitution (V).

Having shown conclusively that prehnitic acid is benzene-1:2:3:5-tetracarboxylic acid, it seemed that mellophanic acid must be benzene-1:2:3:4-tetracarboxylic acid, but in order to be certain it was decided to synthesise this acid.

For this purpose a large amount of 1:4-dimethylnaphthalene was prepared, and this, on oxidation with nitric acid, gave a mixture of acids, from which a tetrabasic acid was separated; this possessed all the properties of Baeyer's mellophanic acid.

When the silver salt of the acid was heated with methyl iodide, a neutral tetramethyl mellophanate (m. p. 133°) was obtained.

Since mellophanic acid is 1:2:3:4-benzenetetracarboxylic acid, it should, in accordance with the usual views on steric hindrance, yield only a diacid ester by the direct process of esterification. This is probably the case, since no trace of neutral tetraethyl mellophanate was produced on heating the acid with alcohol and sulphuric acid. A barium salt was isolated by treatment of the reaction product with baryta and subsequent evaporation, and this gave on titration results which indicated it to be a barium salt of the diacid ester with two or three molecules of water of crystallisation. The direct determination of the water of crystallisation gave entirely anomalous results, and this important point will therefore be re-investigated. It is clear, however, that the acid cannot be completely esterified by the usual process.



As the result of these experiments there can therefore be little doubt that prehnitic acid and mellophanic acid are respectively benzene-1:2:3:5- and -1:2:3:4-tetracarboxylic acids.

It is somewhat difficult to see how Jacobsen (*loc. cit.*) obtained from *isodurene* the acid which he showed to be identical with Baeyer's mellophanic acid, since he prepared his hydrocarbon by the action of methyl iodide and sodium on bromomesitylene. It is hardly likely that any rearrangement of groups would take place during this reaction, as such rearrangement only appears to take place in the presence of aluminium chloride. We are therefore driven to the conclusion that the hydrocarbon used by Jacobsen in his experiments cannot have been mesitylene, and must have consisted mainly of  $\psi$ -cumene.

It has already been mentioned that Töhl (*loc. cit.*) obtained prehnitic acid by the oxidation of prehnitene, which hydrocarbon is prepared by the degradation of pentamethylbenzene by means of sulphuric acid. He, however, offers no proof of the constitution of his hydrocarbon apart from the fact that it was identical with that previously obtained by Jacobsen (*Ber.*, 1886, 19, 1213; 1887, 20, 901). Jacobsen isolated this hydrocarbon by the action of hydrochloric acid on a sulphonamide prepared from durene and by the degradation of pentamethylbenzene, two reactions which offer no proof of constitution, and the only grounds for considering that prehnitene is 1:2:3:4-tetramethylbenzene is because it is isomeric with the hydrocarbon he obtained by the action of methyl iodide and sodium on bromomesitylene, and that it does not give pyromellitic acid on oxidation. If, then, the hydrocarbon obtained by Jacobsen from bromomesitylene is 1:2:3:4-tetramethylbenzene, then prehnitene must be 1:2:3:5-tetramethylbenzene.

Further experiments on this interesting subject are in progress. Unfortunately, the wrong conception of the nature of prehnitic acid and of prehnitene, which has so long prevailed, has led to much confusion in assigning constitutional formulæ on the basis of these substances being 1:2:3:4-substitution derivatives of benzene.

#### EXPERIMENTAL.

##### *Prehnitic Acid (Benzene-1:2:3:5-tetracarboxylic Acid).*

*Mesitylenecarboxylic Acid.*—Bromomesitylene (20 grams) was added to magnesium (24 grams) suspended in dry ether, the magnesium having first been treated with a small amount of methyl iodide in order to render it reactive. A vigorous reaction ensued, and when this had ceased, the mixture was heated on the water-bath until all the magnesium had passed into solution. After being kept cold overnight, a slow stream of dry carbon dioxide was

passed into the ethereal solution of the magnesium compound, when a heavy oil slowly separated. Ice and dilute hydrochloric acid were then added, and the ethereal layer was separated and washed with sodium carbonate solution.

On acidifying the latter solution, a colourless, crystalline precipitate (7.5 grams) separated, which was collected and dried. The mesitylenecarboxylic acid obtained in this way was purified by crystallisation from light petroleum, from which it separated in glistening prisms, possessing the correct melting point, 151—152°. (Found,  $C=72.9$ ;  $H=7.4$ . Calc.,  $C=73.4$ ;  $H=7.3$  per cent.)

*Oxidation of Mesitylenecarboxylic Acid to Prehnitic Acid.*—Mesitylenecarboxylic acid (1 gram) was mixed with 10 c.c. of dilute nitric acid ( $D=1.15$ ), and heated in a sealed tube for eight hours at 170–180°. After removing the nitric acid by evaporation on the water-bath, the prehnitic acid was purified by repeated crystallisation from hydrochloric acid, from which it separated in small prisms. After drying at 100° to remove water of crystallisation, it was analysed. (Found,  $C=46.8$ ;  $H=2.3$ . Calc.,  $C=47.2$ ;  $H=2.3$  per cent.)

Prehnitic acid melts at 252°, previously softening at about 240°, and is converted into the anhydride, melting at 238°, whereas Baeyer (*Annalen*, 1873, 166, 328) states that it begins to melt at 237°, becoming completely liquid at 250°, whilst the anhydride melts at 238°. That it was a tetrabasic acid was shown by titration with standard sodium hydroxide, when it was found that 0.096 neutralised 0.058NaOH, whereas a tetrabasic acid,  $C_{10}H_6O_8$ , should neutralise 0.0608NaOH. When barium chloride was added to an aqueous solution of prehnitic acid and the solution warmed, an immediate precipitate of the barium salt of the acid was obtained. After drying at the temperature of the laboratory for two days, it was analysed, when it was found to have the composition given to the barium salt of prehnitic acid by Baeyer (*Annalen*, 1873, 166, 332):

0.2354 lost 0.0122  $H_2O$  at 100°.  $H_2O=5.2$ .

0.1514 gave 0.0502  $BaSO_4$ .  $Ba=19.4$ .

$(C_{10}H_6O_8)_2Ba \cdot 3H_2O$  requires  $Ba=19.6$ ;  $2H_2O=5.4$  per cent.

The barium salt, when dried at 100°, gave the following result:

0.2197 gave 0.0775  $BaSO_4$ .  $Ba=20.70$ .

$(C_{10}H_6O_8)_2Ba \cdot H_2O$  requires  $Ba=20.8$  per cent.

*Tetramethyl Prehnitate*,  $C_6H_4(CO_2Me)_4$ .—Tetramethyl prehnitate has already been isolated by Baeyer (*Annalen*, 1873, 166, 333) by the action of methyl iodide on the silver salt of the acid. A repetition of this process yielded the ester in beautiful, colourless

needles, which, after crystallisation from methyl alcohol, melted at 108—109° (Baeyer gives 104—109°). (Found, C=54.1; H=4.5. Calc., C=54.2; H=4.5 per cent.)

*Triethyl Hydrogen Prehnitate*,  $C_6H_2(CO_2Et)_3 \cdot CO_2H$ .

This ester, which does not seem to have been previously obtained, is readily formed when prehnitic acid is treated with alcohol and sulphuric acid in the usual manner. It was purified by repeated crystallisation from a mixture of benzene and light petroleum, when it separated in colourless clusters of needles, which melt at about 108—110°:

0.123 gave 0.2625  $CO_2$  and 0.0601  $H_2O$ . C=58.2; H=5.4.

$C_{17}H_{18}O_8$  requires C=58.3; H=5.1 per cent.

*Triethyl hydrogen prehnitate* is readily soluble in most organic solvents with the exception of light petroleum. Its probable constitution has already been discussed in the introduction (p. 1905).

*Dimethyl Dihydrogen Prehnitate*,  $C_6H_2(CO_2Me)_2(CO_2H)_2$ .\*

It has already been pointed out by Meyer and Sudborough (*Ber.*, 1894, 27, 159) that when a methyl-alcoholic solution of prehnitic acid is treated with hydrogen chloride in the cold, only a dimethyl ester is formed. This result has been confirmed, but the melting point of the ester when crystallised from a mixture of acetone and light petroleum was found to be about 191°, and not 176—177°, as stated by them. The silver salt was analysed:

0.0519 gave 0.0225 Ag. Ag=43.3.

$C_{12}H_8O_8Ag_2$  requires Ag=43.5 per cent.

*Mellophanic Acid* (Benzene-1:2:3:4-tetracarboxylic Acid).

*Oxidation of 1:4-Dimethylnaphthalene*.—1:4-Dimethylnaphthalene (2 c.c.), prepared as described by Giovannozzi (*Gazzetta*, 1882, 12, 147), was mixed with 40 per cent. nitric acid (20 c.c.), and heated in a sealed tube at 170—180° for eight hours. The clear solution was evaporated to dryness on the water-bath, when a semi-solid, crystalline mass was obtained, which evidently consisted of a mixture of acids.

In order to separate the mellophanic acid, a somewhat tedious process of purification had to be adopted. The crude acid was dissolved in as little water as possible, and the solution treated with excess of stannous chloride and concentrated hydrochloric acid for two hours on the water-bath. The strongly acid mixture was then

\* By an oversight, Stewart states (*Stereochemistry*, p. 341) that prehnitic acid forms a tetramethyl ester when esterified in the usual manner.

evaporated to dryness, the residue dissolved in water, and the tin precipitated with hydrogen sulphide. After separating the tin sulphide, the solution was again evaporated to dryness, and the mixture of phthalic and mellophanic acids extracted with dry ether in a Soxhlet apparatus, when it was found that the amino-acids, which were present as hydrochlorides, were not dissolved. As preliminary experiments showed it to be a matter of some difficulty to separate the mellophanic and phthalic acids by fractional crystallisation, they were converted into their silver salts in the usual manner, and the dry silver salts were digested with methyl iodide in benzene solution for some hours on the water-bath. After separating from the silver iodide, the benzene was removed, when a viscid oil was obtained, which on trituration with ether partly solidified. The solid ester, which was found to consist of *methyl mellophanate*, was separated and purified by repeated crystallisation from methyl alcohol:

0.124 gave 0.2455  $\text{CO}_2$  and 0.0552  $\text{H}_2\text{O}$ .  $\text{C}=54.0$ ;  $\text{H}=4.9$ .

$\text{C}_{14}\text{H}_{14}\text{O}_8$  requires  $\text{C}=54.2$ ;  $\text{H}=4.5$  per cent.

*Methyl mellophanate*, which does not appear to have been previously described, separates from methyl alcohol in long, glistening needles, melting at  $133-135^\circ$ . It is readily soluble in benzene, ethyl acetate, or acetone, but only sparingly so in ether, light petroleum, or cold methyl alcohol.

In order to obtain the free acid, the methyl ester was hydrolysed in the usual manner with alcoholic potassium hydroxide, and, after removing the alcohol on the water-bath, the solution was acidified, evaporated to dryness, and the acid extracted with ether in a Soxhlet apparatus. The crude acid was purified by crystallisation from hydrochloric acid, when it was found to soften slightly at  $225^\circ$ , and melt and decompose at  $238^\circ$  with formation of the anhydride (compare Baeyer, *loc. cit.*). (Found,  $\text{C}=47.02$ ;  $\text{H}=2.3$ . Calc.,  $\text{C}=47.2$ ;  $\text{H}=2.3$  per cent.) The basicity of the acid was determined by titration with normal sodium hydroxide, when it was found that 0.0648 neutralised 0.0404  $\text{NaOH}$ , whereas a tetrabasic acid,  $\text{C}_{10}\text{H}_4\text{O}_8$ , should neutralise 0.0408  $\text{NaOH}$ .

Mellophanic acid is readily soluble in water or acetone, but only sparingly so in most organic solvents.

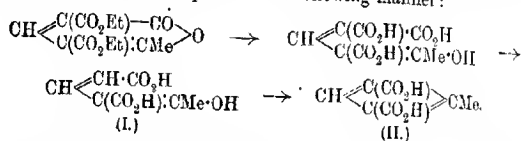
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MADRAS.

## CCIII.—Ethyl 6-Methyl-2-pyrone-3:5-dicarboxylate and its Conversion into Methyltrimesic Acid.

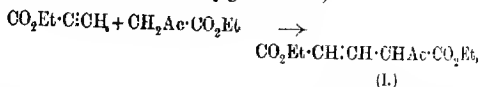
By JOHN LIONEL SIMONSEN.

In a recent communication (Trans., 1908, 98, 1022) the author described the preparation of ethyl 6-methyl-2-pyrone-3:5-dicarboxylate, and pointed out that on hydrolysis with alkaline reagents it gave rise to an acid to which the empirical formula  $C_7H_6O_4$  was given, and it was suggested that this might possibly be 1-methyl- $\Delta^{1:3}$ -cyclobutadiene-2:4-dicarboxylic acid, internal condensation having taken place in the following manner:



Since an acid possessing this constitution would be of theoretical interest from several points of view, further experiments were instituted with the object of subjecting it to a more searching investigation.

It seemed, in the first place, desirable to devise a means of directly synthesising the ethyl ester of  $\alpha$ -acetylglutaconic acid (I), since, if the above reasoning were correct, this ester should, on treatment with suitable reagents, readily be converted into 1-methyl- $\Delta^{1:3}$ -cyclobutadiene-2:4-dicarboxylic acid (II). This synthesis was easily carried out by the condensation of ethyl propiolate and ethyl sodioacetoacetate, when the reaction proceeds quite normally with the formation of ethyl  $\alpha$ -acetylglutaconate,



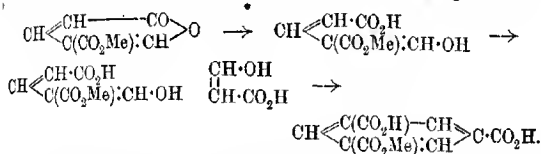
The reaction proceeding on somewhat similar lines to the condensation of ethyl phenylpropiolate and ethyl acetoacetate so exhaustively investigated by Rubemann (Trans., 1899, 75, 251).

At the same time, however, a further reaction takes place, and a small quantity of a crystalline solid was isolated, which melted at  $48^\circ$ , and was found to be identical with the ethyl ester of the acid previously obtained by the hydrolysis of ethyl 6-methyl-2-pyrone-3:5-dicarboxylate (*loc. cit.*, p. 1028). The isolation of this ester was at first thought to be additional evidence in favour of

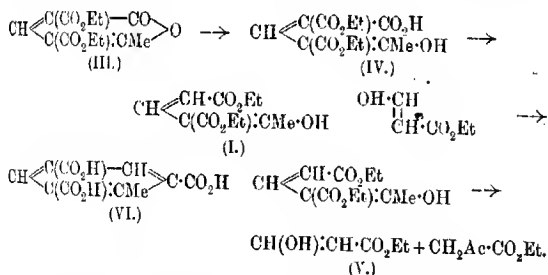
# AND ITS CONVERSION INTO METHYLTRIMESIC ACID. 1911

the original view of the constitution of the acid  $C_7H_6O_4$ , which was, moreover, supported by the fact that ethyl  $\alpha$ -acetylglutaconate, on hydrolysis with barium hydroxide, yielded, besides glutamic acid, a small quantity of the same acid (see p. 1914). As the result of further experiments this view had to be abandoned, and the conclusion was drawn that this acid, supposed to be  $C_7H_6O_4$ , was in all probability a methylbenzenetricarboxylic acid,  $C_{10}H_8O_6$ .

During the course of his classical investigation of coumalinic acid, von Pechmann (*Annalen*, 1891, 264, 293) showed that when the methyl ester of coumalinic acid was hydrolysed with aqueous sodium hydroxide it was converted into the monomethyl ester of trimesic acid, the reaction taking place on the following lines:



Taking these facts into consideration, it appeared probable that the hydrolysis of ethyl 6-methyl-2-pyrone-3:5-dicarboxylate had proceeded in an analogous manner with the formation of a methyltrimesic acid:

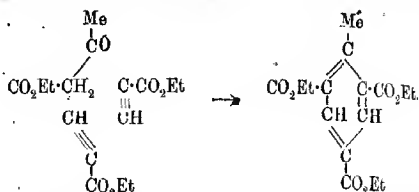


The 2-pyrone (III) is converted, in the first place, into the diethyl ester of  $\alpha'$ -carboxy- $\alpha$ -acetylglutaconic acid (IV), which, with loss of carbon dioxide, passes into ethyl  $\alpha$ -acetylglutaconate (I). Half of the ethyl  $\alpha$ -acetylglutaconate then undergoes decomposition into ethyl formylacetate (V) and ethyl acetoacetate, and the ethyl formylacetate thus generated combines with the unchanged ethyl  $\alpha$ -acetylglutaconate, with loss of two molecules of water and formation of methyltrimesic acid (VI).

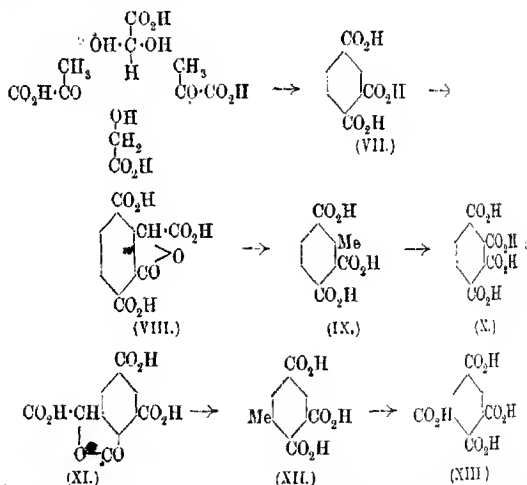
If this constitution be accepted for the acid, the formation of its ethyl ester by the interaction of ethyl propiolate and ethyl aceto-

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acetate is readily explained. It may be assumed that two molecules of ethyl propiolate condense with one of ethyl acetoacetate in accordance with the following scheme:



On examining the literature, it was found that only one other methylbenzenetricarboxylic acid is known. This was obtained by Doebner (*Annalen*, 1900, 311, 136) by the condensation of pyruvic acid and glyoxylic acid and fusion of the resulting phthalidetricarboxylic acid with potassium hydroxide:



Doebner considered that benzene-1:2:4-tricarboxylic acid (VII) was first formed, which then condensed with a further molecule of glyoxylic acid to give phthalidetricarboxylic acid (VIII), and this, on subsequent fusion with potassium hydroxide, gave 1-methylbenzene-2:3:6-tricarboxylic acid (IX). He based this view of the constitution on the fact that on oxidation with potassium permanganate, phthalidetricarboxylic acid gave prebnitic acid, which

is regarded as benzene-1:2:3:4-tetracarboxylic acid (X). Now, since it has been shown in the preceding communication (p. 1904) that prehnitic acid is benzene-1:2:3:5-tetracarboxylic acid (XII), it follows that the acid obtained by Doebner cannot be methylbenzene-2:3:6-tricarboxylic acid.

Probably the condensation described by Doebner proceeds on the following lines. Benzene-1:2:4-tricarboxylic acid (VII) is first formed, and this then condenses with glyoxylic acid to give the someric phthalidetricarboxylic acid (XI), which, on fusion with potassium hydroxide, would give 1-methylbenzene-2:3:5-tricarboxylic acid (XII), and on oxidation with potassium permanganate, prehnitic acid (XIII). This view of the condensation is also more probable on stereochemical grounds.

In order to leave no doubt as to the constitution of the methyltrimesic acid obtained in this investigation, it was oxidised with nitric acid or potassium permanganate, when the tetracarboxylic acid was formed, and was shown to be in every way identical with prehnitic acid (benzene-1:2:3:5-tetracarboxylic acid).

#### EXPERIMENTAL.

##### *Condensation of Ethyl Acetoacetate and Ethyl Propiolate.*

##### *Formation of Ethyl Methyltrimesate and Ethyl $\alpha$ -Acetylglutaconate.*

Sodium (1.3 grams) was dissolved in alcohol, and, after the addition of ethyl acetoacetate (7.8 grams), ethyl propiolate (5.9 grams) was added to the well-cooled solution. Much heat was generated, and the reaction mixture rapidly became deep red. After being kept overnight, water was added, and the oil which separated was dissolved in ether, and the ethereal solution washed, dried, and evaporated. The residual oil was carefully fractionated under diminished pressure (14 mm.), when, after a small amount of unchanged ethyl acetoacetate had passed over, it was found to distil between 210° and 220°. The distillate (3 grams) was cooled in a freezing mixture, when it rapidly solidified, and after draining on porous porcelain it was crystallised from light petroleum, when it melted at 48°:

0.1315 gave 0.3013 CO<sub>2</sub> and 0.0796 H<sub>2</sub>O. C=62.5; H=6.7

C<sub>16</sub>H<sub>18</sub>O<sub>6</sub> requires C=62.7; H=5.9 per cent.

The ethyl methyltrimesate obtained in this manner was found to be in every respect identical with that previously described (*loc. cit.*, p. 1028), and a mixture of the two melted sharply at 48°.

In order to remove any doubt as to the identity of these two substances, a small quantity of the pure ester (1 gram) was hydrolysed with dilute hydrochloric acid, and after removing the excess



of hydrochloric acid by evaporation, the methyltrimesic acid was purified by repeated crystallisation from hot water. After drying at  $110^{\circ}$ , it was analysed:

0.1097 gave 0.2152  $\text{CO}_2$  and 0.0395  $\text{H}_2\text{O}$ .  $\text{C}=53.5$ ;  $\text{H}=4.0$ .

$\text{C}_{10}\text{H}_6\text{O}_6$  requires  $\text{C}=53.6$ ;  $\text{H}=3.6$  per cent.

On melting, it behaved in the manner characteristic of this acid, commencing to sinter at  $268^{\circ}$ , and decomposing completely at  $300^{\circ}$ .

The alkaline mother liquor, from which the ethyl methyltrimesate had been separated, was rendered just acid with dilute hydrochloric acid, when an oil separated. This was dissolved in ether, the ethereal solution washed with dilute sodium carbonate,\* dried, and evaporated, and the residual yellow oil fractionated under diminished pressure (12 mm.), when it was found to distil very constantly at  $158-160^{\circ}$ . Yield 5 grams:

0.1535 gave 0.3244  $\text{CO}_2$  and 0.0997  $\text{H}_2\text{O}$ .  $\text{C}=57.6$ ;  $\text{H}=7.2$ .

$\text{C}_{11}\text{H}_{16}\text{O}_6$  requires  $\text{C}=57.9$ ;  $\text{H}=7.0$  per cent.

Ethyl  $\alpha$ -acetylglutaconate, which does not appear to have been previously described, is a colourless oil, possessing a pleasant ethereal odour. Its alcoholic solution gives with ferric chloride an intense purple-violet coloration.

*Hydrolysis of Ethyl  $\alpha$ -Acetylglutaconate.*—For the hydrolysis of this ester, barium hydroxide was found to yield the most satisfactory results.

Ethyl acetylglutaconate (5 grams) was mixed with a concentrated solution of barium hydroxide [10 grams crystallised  $\text{Ba}(\text{OH})_2$ ], and after boiling for two hours on the sand-bath, the canary-yellow solution was cooled and extracted ten times with pure ether. On removing the ether an oil was obtained which rapidly solidified, and after draining on porous porcelain was crystallised from dry ether, when it was found to separate in two distinct forms, consisting of fine, colourless needles and small, hard, yellow nodules. These were separated, as far as possible, mechanically, and the needles, which weighed less than 0.1 gram, were found to consist of methyltrimesic acid, since they showed the characteristic melting point of this acid, and when esterified with methyl alcohol and sulphuric acid yielded an ester melting at  $107^{\circ}$ .

The main portion of the acid, which separated in hard, yellow nodules, was purified by repeated crystallisation from ether with the aid of animal charcoal, when it was obtained in colourless prisms, melting at  $138^{\circ}$ , and evidently consisted of glutaconic acid, which melts at this temperature (Buchner, *Ber.*, 1890, 23, 703). (Found,  $\text{C}=45.9$ ;  $\text{H}=4.7$ . Calc.,  $\text{C}=46.2$ ;  $\text{H}=4.6$  per cent.)

\* The sodium carbonate washings, on acidification, yielded a small amount of a viscid oil which was not further investigated.

*Methyltrimesic Acid*,  $\text{CH}_3\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$ .

The properties of methyltrimesic acid have already been described (*loc. cit.*, p. 1027), but in view of the somewhat unsatisfactory analytical data obtained, further experiments were instituted with the view of obtaining this acid in a purer state. As it was not readily purified by repeated crystallisation from hot water, the acid was dissolved in a slight excess of sodium carbonate and oxidised with a dilute solution of potassium permanganate in the cold until a permanent pink colour was obtained. After removing the excess of potassium permanganate with sulphur dioxide, the manganese dioxide was removed, and the alkaline solution concentrated and acidified. The precipitated acid was collected and repeatedly crystallised from hot water, from which it separates, when pure, in long, prismatic needles, melting at the temperature previously given:

0.1606 gave 0.3146  $\text{CO}_2$  and 0.0532  $\text{H}_2\text{O}$ .  $\text{C}=53.5$ ;  $\text{H}=3.7$ .

0.1392 „ 0.2747  $\text{CO}_2$  and 0.0459  $\text{H}_2\text{O}$ .  $\text{C}=53.8$ ;  $\text{H}=3.6$ .

$\text{C}_{10}\text{H}_6\text{O}_6$  requires  $\text{C}=53.6$ ;  $\text{H}=3.6$  per cent.

The silver salt separates as a caseous, white precipitate when silver nitrate is added to a faintly alkaline solution of the ammonium salt. After drying at  $100^\circ$ , it was analysed:

0.1915 gave 0.114 Ag.  $\text{Ag}=59.5$ .

$\text{C}_{10}\text{H}_6\text{O}_6\text{Ag}_3$  requires  $\text{Ag}=59.4$  per cent.

*Methyl Methyltrimesate*.—This ester, which has been previously described, when pure melts at  $107^\circ$ , and not at  $106^\circ$  (*loc. cit.*, p. 1028). A pure specimen was prepared for the determination of the refractive index; on analysis it gave the following figures:

0.1349 gave 0.2888  $\text{CO}_2$  and 0.0626  $\text{H}_2\text{O}$ .  $\text{C}=58.4$ ;  $\text{H}=5.1$ .

$\text{C}_{13}\text{H}_{14}\text{O}_6$  requires  $\text{C}=58.6$ ;  $\text{H}=5.2$  per cent.

Methyl methyltrimesate is also obtained in a yield of 96.5 per cent. when methyltrimesic acid is esterified by the method used by Meyer and Sudborough (*Ber.*, 1894, 27, 1591). The acid (0.5 gram) was dissolved in methyl alcohol (10 c.c.), and the solution saturated in the cold with hydrogen chloride. The acid immediately separated out, but on keeping in the cold slowly redissolved, and after twelve hours the liquid was filled with a mass of felted needles. These were dissolved in ether, when 0.56 gram of the ethyl ester was obtained. This result is of some interest, as, from stereochemical considerations, it seemed unlikely that the trimethyl ester would be formed, especially since under similar conditions benzoic acid only yields a dimethyl ester (see p. 1908).

Mr. R. T. Hardman kindly carried out a molecular-weight deter-

mination of this ester by the cryoscopic method, benzene being used as the solvent

0.267, in 17.537 benzene, gave  $\Delta t = -0.3^\circ$ . M.W. = 253.7.  
0.4052, in 17.57 " "  $\Delta t = -0.456^\circ$ . M.W. = 253.0.

$C_{15}H_{14}O_6$  requires M.W. = 266.

I am much indebted to Dr. Ida Smedley for very kindly determining the refractive power of this ester. The determination was carried out in chloroform solution:

Percentage strength of solution.	$M_D$	$M_R$	$M_Y$	$M_{Y-a}$
6.5986	65.47	67.77	68.79	3.32

Calculated value  $C_{15}H_{14}O_6 \cdot 311 = 63.23$ .

It seems likely that the high value is due to the conjugation of the carbonyl groups with the benzene ring.

*Distillation of the Barium Salt of Methyltrimelic Acid.*—The barium salt (30 grams) was mixed with barium oxide (120 grams), and carefully distilled from a retort, when an oil slowly passed over. This was purified by repeated distillation over sodium, when it was found to boil constantly at  $110^\circ$ , and evidently consisted of nearly pure toluene. (Found, C=90.7; H=8.7. Calc., C=91.3; H=8.7 per cent.)

#### *Oxidation of Methyltrimelic Acid to Prehnitic Acid.*

I. *With Nitric Acid.*—Methyltrimelic acid (2 grams) was mixed with 40 per cent. nitric acid (20 c.c.), and heated in a sealed tube for six hours at  $170-180^\circ$ . The clear solution was evaporated to dryness, and the solid acid thus obtained was purified by repeated crystallisation from hydrochloric acid, when it separated in microscopic prisms. After drying at  $100^\circ$ , it was analysed. (Found, C=47.2; H=2.5. Calc., C=47.2; H=2.3 per cent.) Prehnitic acid obtained in this manner melted at  $250-251^\circ$ , softening slightly at  $247^\circ$ , with formation of the anhydride, which melted at  $238^\circ$ . It was found to be identical in every way with prehnitic acid, obtained by the oxidation of mesitylenecarboxylic acid (see p. 1907). The basicity of the acid was determined by titration with standard sodium hydroxide, when 0.1095 of the acid neutralised 0.0685NaOH, whereas this amount of a tetrabasic acid,  $C_{16}H_6O_8$ , should neutralise 0.0685NaOH.

II. *With Potassium Permanganate.*—In carrying out this oxidation, methyltrimelic acid (5 grams) was dissolved in a slight excess of dilute sodium carbonate solution, and after the addition of potassium permanganate (10 grams) dissolved in water (500 c.c.) the mixture was boiled in a reflux apparatus for twelve hours when the oxidation was complete. After removing the manganese

dioxide, the alkaline solution was concentrated on the water-bath, acidified, and extracted several times with ether, the ethereal solution being dried and evaporated. The crystalline acid thus obtained was purified by crystallisation from hydrochloric acid, when it was found to melt at  $250-251^{\circ}$ , with formation of the anhydride, which melted at  $238^{\circ}$ . This acid was in every way identical with that obtained in the oxidation with nitric acid. The silver salt separates as a caseous, white precipitate on the addition of silver nitrate to a slightly alkaline solution of the ammonium salt. (Found,  $C=17.2$ ;  $H=0.7$ ;  $Ag=62.9$ . Calc.,  $C=17.6$ ;  $H=0.3$ ;  $Ag=63.4$  per cent.)

In order to leave no doubt as to the identity of this acid with prehnitic acid, the characteristic barium salt was prepared by the addition of barium chloride to a warm aqueous solution of the acid. After drying for two days in the air it was analysed. (Found,  $Ba=19.6$ ;  $H_2O=5.0$ .  $(C_{10}H_5O_3)_2Ba \cdot 3H_2O$  requires  $Ba=19.6$ ;  $2H_2O=5.4$  per cent.) It was also analysed after being dried at  $100^{\circ}$ . (Found,  $Ba=20.6$ .  $(C_{10}H_5O_3)_2Ba \cdot H_2O$  requires  $Ba=20.8$  per cent.)

Tetramethyl prehnitate was prepared in the usual manner by the action of methyl iodide on the silver salt of the acid, and after crystallisation from methyl alcohol melted at  $108-109^{\circ}$ . (Found,  $C=53.7$ ;  $H=4.6$ . Calc.,  $C=54.2$ ;  $H=4.5$  per cent.)

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed much of the expense of this and the preceding communication.

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MANCHESTER.

#### CCIV.—*The Volatile Constituents of Coal.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

This investigation into the nature of the "volatile constituents" of coal has been undertaken in connexion with experiments now being conducted by the Mining Association of Great Britain. These experiments—"the British Coal Dust Experiments"—have for their object the study of the phenomena occurring during the explosive combustion of mixtures of fine coal dust and air, with a view to discover a means of preventing such explosions.

An investigation into the nature of the volatile constituents of coal is of particular value in connexion with such a problem, because of the obvious relationship that exists between the behaviour

on heating of the volatile matter contained in any sample of coal and the degree of inflammability of the coal dust.

By determining such factors as (a) the temperature at which gas is most readily evolved, (b) the stage in the heating at which the most inflammable mixture of gases makes its appearance, and (c) the shortest time of heating that will allow any gas at all to be distilled, it should be possible to draw a distinction between dusts of different degrees of inflammability or liability to propagate explosion.

The interest that attaches to the study of the action of heat on coal, however, is not confined to any particular problem, and although in carrying out the present investigation we have had the problem of coal dust explosions alone in mind, we believe that the experimental methods adopted render our results of more wide spread application.

We hope ultimately to obtain definite information regarding the composition and chemical constitution of coal.

#### *Destructive Distillation of Coal at Different Temperatures.*

This part of our investigations, the ultimate object of which is the elucidation of the nature of "coal," yields only a little information in that direction when considered by itself. We find it necessary, therefore, to reserve our conclusions regarding the composition of coal for a future communication, and merely to indicate the bearing that this part of our work has on the subject.

The principal facts brought to light by the distillation of different samples of coal at different temperatures are as follows:

1. With all coals, whether bituminous, semi-bituminous, or anthracite, there is a well-defined decomposition point, at a temperature lying between  $700^{\circ}$  and  $800^{\circ}$ , which corresponds with a marked increase in the quantity of hydrogen evolved. With bituminous coals, the increase in the quantity of hydrogen evolved falls off at temperatures above  $900^{\circ}$ , but with anthracitic coals it is maintained up to  $1100^{\circ}$ .
2. Evolution of hydrocarbons of the paraffin series ceases practically entirely at temperatures above  $700^{\circ}$ .
3. Ethane, propane, and butane, and, probably, higher members of the paraffin series form a large percentage of the gases evolved at temperatures below  $450^{\circ}$ .

From these facts it may be concluded that coal of whatever geological age contains a compound which undergoes decomposition at temperatures above  $700^{\circ}$  (under atmospheric pressure), and yields hydrogen as its principal gaseous product. It seems probable, also

that this same compound is responsible for the hydrocarbons of the paraffin series that make their appearance at low temperatures. The technical application of our results is readily apparent. In the manufacture of lighting gas there is, as yet, no decided opinion as to the best carbonising temperature to use, nor has the influence that temperature has on the nature and quantity of the products of distillation been thoroughly investigated.

The efficiency of a boiler is largely dependent on the quantity and the nature of those constituents of coal that can be gasified at a comparatively low temperature. The chief loss of efficiency when generating steam by the combustion of coal arises from the cooling effect of the boiler surface on the gases evolved from the coal, whereby their temperature is reduced below the point necessary for complete combustion. According to the nature of the coal, the temperature at which gases can be distilled, and the rate at which the distillation takes place, varies; and the effect of cooling by the boiler surface will also vary with the nature of the gases evolved. It is possible that on the last factor the smoke-producing tendencies of some varieties of coal largely depend.

Previous work of this nature appears to be very scanty, but since this investigation was begun an account has appeared in the technical journals of some work that has been carried out by H. C. Porter and F. K. Ovitz, of the Technological Branch of the United States Geological Survey during 1907-1908 (*J. Gaslighting*, 1908, 107, 343), which is very similar in character to that described in this part of our work, though done with a different object in view.

Details are given of the distillation at different temperatures of two samples of coal, as follows:

*Ziegler Coal, Illinois.*

Moisture .....	7.67 per cent.						
Volatile matter.....	30.33 "						
Fixed carbon.....	54.32 "						
Ash.....	7.63 "						
Retort temperature (°).....	500	600	700	800	900	1000	1100
Maximum temperature in coal (°) .....	390	480	585	685	811	920	1026
Gases evolved from 10 grams (c.c.) .....	130	535	978	1550	2335	2700	3120
<i>Analysis of Gas.</i>							
CO.....	21.0	6.7	5.7	3.6	2.2	2.5	1.7
" Illuminants" .....	5.6	4.3	3.6	3.0	3.0	3.6	3.7
CO .....	13.3	13.9	19.1	18.7	14.5	14.4	13.9
H <sub>2</sub> .....	—	14.2	24.1	38.5	48.7	52.6	54.6
CH <sub>4</sub> .....	16.4	34.1	30.0	27.1	20.7	18.1	18.9
C <sub>2</sub> H <sub>6</sub> .....	14.8	13.6	7.7	5.0	6.0	3.9	4.2
N <sub>2</sub> .....	28.9	13.2	9.8	7.1	4.9	4.9	6.0

*Connellsville Coal, Pocahontas.*

Moisture .....	1.10 per cent.
Volatile matter.....	30.87 "
Fixed carbon.....	60.35 "
Ash .....	7.88 "

Retort temperature (°).....	500	600	700	800	900	1000	1100
Maximum temperature in coal (°) .....	390	474	539	705	812	922	1010
Gas evolved from 10 grams (c.c.) .....	150	625	1220	1723	2080	2200	3530

*Analysis of gas.*

CO <sub>2</sub> .....	11.2	3.4	2.7	2.0	1.1	1.1	1.0
"Illuminants".....	5.3	5.7	3.8	4.3	4.7	4.3	4.9
CO .....	5.2	5.3	5.3	7.0	7.2	5.9	7.0
H <sub>2</sub> .....	—	10.9	27.0	38.1	52.0	56.0	58.2
CH <sub>4</sub> .....	4.5	41.2	36.2	36.0	25.2	24.4	21.5
C <sub>2</sub> H <sub>6</sub> .....	32.5	18.9	12.9	9.5	7.1	3.0	3.8
N <sub>2</sub> .....	41.3	14.6	12.1	3.1	2.7	5.3	3.6

The "illuminants" are taken to be the benzene and the ethylene hydrocarbons, whilst the figure for ethane includes all higher paraffin hydrocarbons calculated as C<sub>2</sub>H<sub>6</sub>.

The distillations were conducted in each case on 10 grams of air-dried coal in an atmosphere of nitrogen, which was passed through the retort before heating until the exit gases contained less than 1 per cent. of oxygen.

The most important conclusion drawn by Porter and Orvitz from their work is that the nature of the volatile products distilled from different samples of coal at low temperatures in the early stages of heating varies in accordance with the smoke-producing tendencies of the coal.

They include among the smoke-producing constituents tar, benzene, ethylene, and the higher homologues of methane. From the figures reproduced here it will be seen that the Connellsville yields a larger quantity of these gases than the Ziegler coal at low temperatures, while it is found in practice that there is a greater difficulty in burning coals of the Connellsville type without smoke.

We are inclined to believe that the smoke-producing constituents consist practically entirely of the higher hydrocarbons of the paraffin series; for we have isolated small quantities of propane and butane from the gases evolved from coal at low temperature, and have obtained evidence of the presence of the higher members of the series. These gases readily decompose at temperatures below 600°, depositing carbon; whilst ethylene yields very little carbon on decomposition at this temperature.

The general trend of the results is in agreement with our own, although it is impossible to make any direct comparison owing to

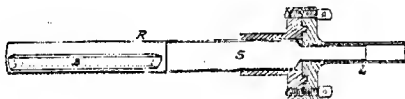
differences in the manner of distillation. We are inclined, however, to doubt the complete absence of hydrogen in the gases distilled at 500°, and we cannot regard the methods of gas analysis employed by Porter and Oviatt as being entirely satisfactory.

#### EXPERIMENTAL.

*The Coal Samples.*—The validity of comparison between one distillation and another depends to a very great extent on the obtaining of a uniform and representative sample of coal. The samples were procured in each case by pulverising about 150 kilograms of screened nut coal in a special form of disintegrator, and collecting during the operation about 1 kilogram of the fine dust formed. This dust was then passed through a sieve with 240 meshes per linear inch, and stored in screw-top bottles. About 75 per cent. of the pulverised coal passed through such a mesh.

*The Method of Distillation.*—Two grams of coal, dried at 107°, are intimately mixed with 3 grams of white sand, which has pre-

FIG. 1.



Platinum retort and connexions.

viously been ignited. The mixture is placed in a thin platinum boat (*B*, Fig. 1) 13 cm. long, which slides easily into a retort, *R*, which consists of a platinum tube 21.5 cm. long and of 1.7 cm. internal diameter.

This tube is silver-soldered into a gun-metal collar with a wide flange, whilst a similar flange carrying a short length of gun-metal leading-tube (*L*) of 1 cm. bore is bolted on to the retort by six small screws through the flanges. The face connected with the leading-tube has a projecting ring midway between the centre and the circumference, which is pressed into a corresponding sunk ring on the retort face, using a washer of asbestos and graphite. A perfect vacuum-tight connexion can be made in this manner.

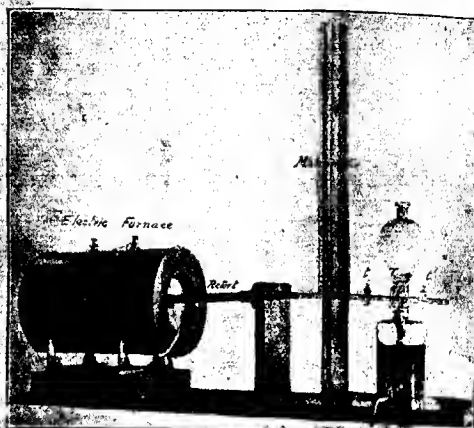
Before this connexion is made, a tar-scrubber (*S*) is fitted into the mouth of the retort. This scrubber consists of a platinum tube packed with ignited asbestos fibre and open at both ends. It is 1.5 cm. in diameter for 8 cm. of its length, and then narrows into a tube 0.8 cm. in diameter and 5.5 cm. long. These dimensions allow of its occupying the position shown in Fig. 1, the wide portion making a good sliding fit inside the retort.



The connexion to the retort having been made, the gun-metal leading-tube is joined by stout rubber pressure tubing to a mercury manometer and a 2-litre gas-holder. The retort and connexions are then exhausted of air through the glass taps *t*, *T*, *t'*, the tap *t* closed, and *T*, which is a three-way tap, turned so as to make connexion with the gas-holder and the retort as soon as *t* is opened (Fig. 2).

The whole arrangement is mounted on a wooden support, and runs on wheels so as to allow of the retort being quickly pushed

FIG. 2.

*Distillation apparatus.*

into the furnace, which has been previously brought to the experimental temperature.

As soon as the pressure of the gases evolved is equal to the atmospheric pressure, the tap *t* is opened, and the gas at once passes into the holder and is collected. Heating is continued for a definite period, usually seventy-five minutes, and the retort then withdrawn and allowed to cool. The gases remaining in the retort are exhausted by means of a mercury pump, and added to the main bulk in the gas-holder. The gun-metal joint is then disconnected, the tar-scrubber and the boat removed and weighed, and the gases analysed.

In this manner the following data are obtained: (1) The rate of evolution of gas; (2) the volume of gas evolved; (3) the com-

position of this gas; (4) the quantity of tar formed; and (5) the total loss in weight of the coal, that is, the total volatile matter.

*The Distillation Furnace.*—In order to make sure that the retort shall be heated evenly throughout its length, the tube furnace employed is a platinum-wound electric resistance furnace, which, with a current of a little more than 1 ampere at 200 volts, can attain a temperature of 1400°. The furnace was tested by means of a thermo-couple for each centimetre of its length to make sure that the coal would be in the zone of highest and of uniform temperature when the retort was inserted.

The temperatures are measured by means of a platinum and platinum-rhodium thermo-couple, which runs through the length of the furnace (the junction being in the centre), and is insulated by an unbroken length of silica quill tubing.

*The Gas Analyses.*—The gases are collected over a mixture of equal parts (by volume) of glycerol and water previously saturated with coal gas. The gases do not dissolve in such a mixture to any appreciable extent, and its use is more convenient than that of mercury.

The gas analyser have been carried out with a modification of the Bone and Wheeler apparatus (*J. Soc. Chem. Ind.*, 1908, 27, 10). With this apparatus the absorptions are carried out over mercury in one absorption vessel with a comparatively small volume of the particular reagent, which is always used fresh and is at once discarded after use, the absorption vessel being rinsed out with dilute sulphuric acid before the next reagent is used.

The reagents that we have employed for the different constituents are as follows, the absorptions being made in the order named:

Gas.	Reagent.
Ammonia .....	Dilute sulphuric acid (10 per cent.).
Benzene .....	Concentrated sulphuric acid (D 1.9).
Hydrogen sulphide .....	Acidified solution of copper sulphate.
Carbon dioxide .....	Potassium hydroxide solution.
Oxygen .....	Strongly alkaline pyrogallol acid.
Acetylene .....	Ammoniacal silver chloride solution.
Ethylene .....	Bromine water with potassium bromide.
Carbon monoxide .....	Ammoniacal cuprous chloride solution.

The gas remaining after these absorptions is passed into a set of exhausted glass bulbs containing "oxidised" palladium precipitate heated in a water-bath to 90°. Heating is continued during ten minutes, the bulbs allowed to cool, and the residual gases withdrawn by means of a mercury pump and measured. The change in volume observed is taken to be due to removal of hydrogen by the palladium.

An explosion analysis is then made in the usual manner.

The details of experiments with four samples of coal are given in the tables following.

The distillation temperatures recorded are the retort temperatures, not those existing in the coal. The temperature in the coal itself reaches the retort temperature at the end of two minutes; thus, in a special experiment made to test this point, in which a thermo-couple was embedded in the coal itself, the temperatures recorded immediately after the insertion of the retort in the furnace were as follows:

	Retort.	In coal.
At beginning .....	330°	400°
After half a minute .....	790	580
After one minute .....	815	780
After one and a half minutes ..	835	835
After two minutes .....	840	840

The records of the rate of evolution of gas are taken from the moment that the pressure in the apparatus reaches atmospheric pressure. The volumes are not corrected for variation in temperature and pressure.

The total quantity of gas evolved is calculated per gram of ash-free dry coal as "nitrogen-free" gas at 0° and 760 mm.

The different constituents of the gas mixtures are calculated as percentages of the nitrogen-free mixture. From 1 to 4 per cent. of nitrogen is usually found in the mixtures, but since this may partly be due to the presence of traces of air in the retort connexions, or to error in analysis, it is thought best for the purpose of comparison to assume that the gases are free from nitrogen.

The quantities of tarry matter and of total volatile matter are calculated as percentages of the ash-free dry coal.

#### *Coal A (Bituminous).*

Coal from the Alkofts Silkstone Seam. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon .....	80.50	} Per cent. of ash-free dry coal.
Hydrogen .....	5.45	
Oxygen .....	9.70	
Nitrogen .....	1.42	
Sulphur .....	2.93	

and it contained 5.51 per cent. of ash.

TABLE I.

*Rate of Evolution of Gas at Different Temperatures.*

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.								
	600°	700	750	800	900	1000	1050	1100	
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	
1st minute .....	40	50	90	145	225	300	375	} 550 in first three minutes.	
2nd " .....	25	25	45	75	125	145	90		
3rd " .....	15	25	25	35	50	30	25		
4th " .....	10	15	15	25	25	25	15		10
5th " .....	5	10	10	20	20	5	10		5
Total first 5 minutes.	95	125	185	300	445	505	515	565	
Next 5 minutes .....	22	30	30	60	50	60	25	30	
" 5 " .....	13	15	25	25	15	15	15	5	
" 15 " .....	25	35	35	27	20	25	15	25	
" 15 " .....	15	10	15	13	15	15	15	15	
" 30 " .....	10	10	5	10	10	25	15	5	

With distillation : at 450° and 500°, 25 c.c. and 60 c.c. respectively were evolved, the total duration of heating being two hours.

TABLE II.

*Volatile Constituents Evolved at Different Temperatures.*

Per cent. ash-free, dry coal.

	Distillation temperature.									
	450°	500	600	700	750	800	900	1000	1050	1100
Total volatile matter :										
9.10	18.79	28.37	32.30	34.04	36.30	38.05	38.30	38.80	38.85	
Tarry matter :										
4.29	9.05	13.68	14.08	16.20	13.50	12.25	10.40	10.90	9.00	

The condensed products at distillation temperatures of 450° and 500° were light-coloured oils.

The coke remaining after all distillations up to and including that at 800° was dull black in colour, and had a tarry odour. Above this temperature the coke was greyish-white and lustrous, and free from any odour of tar.

TABLE III.

Percentage Composition of Gas Evolved at Different Temperatures  
Calculated as "nitrogen-free" gas.

	Distillation temperature.									
	450°	500	600	700	750	800	900	1000	1050	1100
NH <sub>3</sub> ...	4.70	1.35	1.40	1.60	5.20	{ 1.00 1.00 }	3.65	3.65	3.90	
C <sub>2</sub> H <sub>6</sub> ...	8.60	4.85	5.20	3.40		{ 3.65 3.30 }	1.65	1.65	1.70	
CO...	10.95	3.60	3.50	4.05	3.30	1.70 1.70				
C <sub>2</sub> H <sub>4</sub> ...	nil	0.35	—	0.40	—	—	—	0.50	—	nil
C <sub>2</sub> H <sub>2</sub> ...	0.85	1.65	1.80	1.05	0.75	0.90	1.40	1.65	1.55	1.65
CO...	8.75	6.45	7.10	7.00	9.40	11.85	13.65	16.10	14.80	15.85
H <sub>2</sub> ...	7.00	16.60	26.60	32.70	41.65	48.55	55.70	58.40	58.55	58.65
OH...	25.00	37.55	35.20	34.60	29.90	28.10	16.95	17.55	17.05	17.60
C <sub>2</sub> H <sub>4</sub> ...	34.10	27.60	19.20	14.30	9.80	6.25	6.00	3.55	4.85	3.40

TABLE IV.

Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at  
Different Temperatures, and Volumes of Principal Constituents.

	Distillation temperature.									
	450°	500	600	700	750	800	900	1000	1050	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas.	12.00	29.90	99.00	124.00	154.00	218.00	268.0	305.0	315.0	327.0
H <sub>2</sub> .....	0.84	5.00	26.4	40.55	64.20	105.80	149.3	172.0	178.0	186.2
CH <sub>4</sub> .....	3.00	11.25	34.9	42.90	46.05	56.90	45.5	53.5	53.6	57.5
C <sub>2</sub> H <sub>6</sub> .....	4.10	8.25	19.0	17.70	15.10	13.30	16.1	10.3	15.3	11.1
CO .....	1.04	1.95	7.0	9.80	14.45	25.80	36.6	46.0	48.6	51.3
C <sub>2</sub> H <sub>4</sub> .....	0.10	0.45	1.7	2.00	1.15	1.95	3.7	5.0	4.9	6.0

The numbers for hydrogen, methane, ethane, and carbon monoxide are shown graphically in Fig. 3.

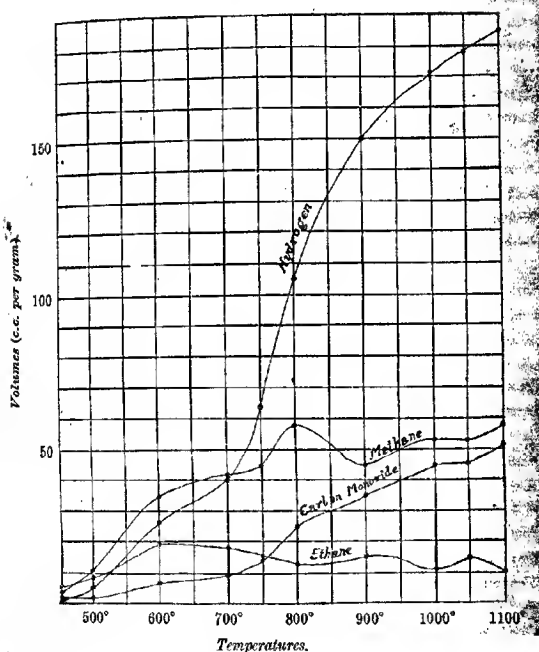
All the data obtained indicate that there is a "critical" period in the decomposition of the coal between 700° and 800°. The rate of evolution of gas and the total quantity evolved per gram are nearly double at 800° what they are at 700°; the curve for total volatile matter shows a marked change in character, becoming steeper at the point given by the distillation at 750°; the quantity of tarry products reaches a maximum at 750°; whilst the total quantity of hydrogen evolved is more than doubled between 700° and 800°, the change in the character of the curve being very marked (Fig. 3).

A noteworthy fact regarding the composition of the gases is the presence of a high percentage of ethane in the gases evolved at low temperatures, the percentage decreasing progressively with

higher temperatures of distillation. It will be observed, however, that the actual quantity of ethane varies very little with the temperature of distillation after 600°; and it would appear probable that such quantities as are found to exist in the products of the high-temperature distillations are evolved only during the initial period of slow heating up of the coal which necessarily takes place.

FIG. 3.

COAL A.



when the retort is first pushed into the furnace; and that their appearance in the final products is due to their having been swept out of the retort as the rate of evolution of gas increased, and thus

\* It may here be remarked that ethane exists, in quantity up to 5 per cent., in many samples of ordinary lighting gas; a fact which appears to have escaped general notice, and may account, to a certain extent, for the discrepancy so often observed between the calorific value of lighting gas as determined directly and as calculated from analysis.

(Trans., 1909, 95, 1211), the thermal decomposition of ethane is fairly rapid at  $675^{\circ}$ , and at  $1000^{\circ}$  it is practically instantaneous.

The greatest interest attaches to the quantities of hydrogen and of methane found in the gases. At a temperature of  $750^{\circ}$  there is a sudden increase in the total quantity of hydrogen evolved, and the rate of increase is maintained fairly regularly up to  $900^{\circ}$ .

The question arises as to the nature of the reaction responsible for the evolution of this hydrogen. It cannot be, as has been suggested, that hydrogen is produced at the expense of methane; for the total quantity of the latter gas evolved undergoes very little variation, as is shown in table IV, and graphically in Fig. 3.

It might, however, be contended that the fact that the total quantity of methane evolved undergoes little or no variation after a distillation temperature of  $750^{\circ}$  has been attained, is due to the fact that, at each of the higher distillation temperatures, a given quantity is evolved during the initial stage of heating up of the coal; and that as soon as the temperature in the coal rises above a certain point, any further methane evolved is at once resolved into its elements.

Bone and Coward have shown (*loc. cit.*, p. 1206), however, that methane is comparatively stable when heated in a porcelain tube at temperatures below  $1100^{\circ}$ , only about 50 per cent. being decomposed after one minute's heating; whilst at a temperature of  $735^{\circ}$  the retort temperature in our experiments corresponding with the maximum rate of evolution of hydrogen—10 per cent. only was decomposed at the end of an hour's heating.

Moreover, the carbon deposited during the course of the thermal decomposition of methane is a characteristic hard and lustrous variety, almost metallic in appearance, and can readily be detected. We have been unable to detect the slightest trace of such carbon deposit below  $900^{\circ}$  distillation temperature, although at  $1050^{\circ}$  a quantity just sufficient to weigh could be brushed off the sides of the platinum boat and retort.

Hydrocarbons of the ethylene series yield a greater quantity of methane than of hydrogen on decomposition below  $800^{\circ}$ , and in any case the quantity present is insufficient to account for the large increase in hydrogen.

We are inclined to believe that, at a temperature of about  $750^{\circ}$ , one or more of the higher hydrocarbons of the paraffin series undergoes rapid decomposition, yielding chiefly hydrogen and carbon; decomposition at lower temperatures yielding methane, and hydrogen. We are studying this point in connexion with another part of this investigation.

*Coal C (Bituminous).*

Coal from Abertillery, South Wales. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon .....	85.72	} Per cent. of ash-free, dry coal
Hydrogen .....	4.93	
Oxygen .....	7.34	
Nitrogen .....	1.09	
Sulphur .....	0.92	

and contained 7.65 per cent. of ash.

TABLE I.

*Rate of Evolution of Gas at Different Temperatures.*

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.					
	600° c.c.	700 c.c.	800 c.c.	900 c.c.	1000 c.c.	1100 c.c.
During 1st minute .....	—	60	100	200	320	475
" 2nd " .....	—	35	70	105	130	45
" 3rd " .....	—	25	40	50	25	30
" 4th " .....	—	20	25	15	15	5
" 5th " .....	—	10	15	10	10	5
Total first 5 minutes...	70	150	250	380	500	560
Next 5 minutes.....	30	30	50	50	45	40
" 5 " .....	20	25	50	20	10	5
" 15 " .....	20	20	30	25	20	15
" 15 " .....	10	20	20	6	15	5
" 30 " .....	10	5	15	20	10	5

With a distillation temperature of 500°, 65 c.c. were evolved during two hours.

TABLE II.

*Volatile Constituents Evolved at Different Temperatures.*

Per cent. ash-free, dry coal.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
Total volatile matter .....	13.46	21.17	25.63	28.94	30.14	31.36	31.50
Tarry matter .....	7.00	10.02	7.36	10.56	9.67	9.19	8.21

The coke remaining after the distillations at 900°, 1000°, and 1100° was greyish-white and lustrous; that remaining after the distillation at 500°, 600°, 700°, and 800° was dark and compact. This coal does not swell so much on coking as does coal A.



TABLE III.

*Percentage Composition of Gas Evolved at Different Temperatures,  
Calculated as "nitrogen-free" gas.*

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
NH <sub>3</sub> .....	2.00	0.70	1.10	0.85	nil	nil	nil
C <sub>2</sub> H <sub>4</sub> .....	4.40	3.55	2.40	2.00	1.85	1.45	2.25
CO .....	3.95	3.20	3.40	2.50	1.65	1.20	1.40
C <sub>2</sub> H <sub>2</sub> .....	0.45	0.30	0.30	0.05	0.05	0.10	0.50
C <sub>2</sub> H <sub>6</sub> .....	0.90	1.05	0.05	0.70	1.95	1.45	1.55
CO .....	4.70	6.45	7.45	9.80	11.25	13.55	18.00
H <sub>2</sub> .....	8.00	25.05	34.75	50.80	57.05	59.80	60.70
CH <sub>4</sub> .....	64.50	47.20	46.25	28.60	21.80	19.25	18.80
C <sub>2</sub> H <sub>6</sub> .....	11.05	12.45	4.25	4.70	5.25	3.10	1.80

TABLE IV.

*Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at  
Different Temperatures, and Volumes of Principal Constituents.*

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas ...	33.50	83.00	135.00	208.00	254.00	296.00	312.00
H <sub>2</sub> .....	2.70	20.80	46.95	105.70	144.95	177.00	180.45
CH <sub>4</sub> .....	21.60	39.20	62.45	50.50	55.50	57.25	58.35
C <sub>2</sub> H <sub>6</sub> .....	3.70	10.35	5.75	9.80	13.35	9.15	5.00
CO .....	1.65	5.35	10.05	20.35	28.55	40.15	40.55

The general behaviour of this coal on heating is similar to that of coal A. This is seen most clearly on comparing curves showing the volumes of the constituent gases evolved at the different temperatures of distillation.

A sudden increase in the quantity of hydrogen evolved is again apparent at a temperature lying between 700° and 800°, whilst the quantity of methane evolved remains remarkably constant at all temperatures above 700°. The presence of "methane-carbon" could only be detected after the distillations at 1000° and 1100°.

The quantity, and the percentage, of ethane evolved is considerably less at all temperatures than in the case of coal A.

#### Coal D (Semi-bituminous).

Coal from Penrhycyber, South Wales. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon .....	90.72	} Per cent. of ash-free, dry coal.
Hydrogen .....	4.23	
Oxygen .....	1.25	
Nitrogen .....	2.99	
Sulphur .....	0.81	

and it contained 3.5 per cent. of ash.

TABLE I.

*Rate of Evolution of Gas at Different Temperatures.*

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.				
	700°	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.
During 1st minute .....	—	90	175	300	550
2nd " .....	—	60	120	150	50
3rd " .....	—	40	60	25	15
4th " .....	—	25	30	25	10
5th " .....	—	15	15	10	10
Total first 5 minutes.....	100	230	400	510	635
Next 5 minutes.....	25	55	45	40	20
5 " .....	20	30	15	10	10
15 " .....	20	50	30	10	10
15 " .....	10	15	15	5	5
80 " .....	10	10	10	5	5

With distillations at 500° and 600°, 30 c.c. and 114 c.c. respectively were evolved, the total duration of heating being two hours.

TABLE II.

*Volatile Constituents Evolved at Different Temperatures.*

Per cent. ash-free, dry coal.

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
Total volatile matter	3.54	7.71	10.47	14.40	16.75	17.84	19.00
Tarry matter .....	0.99	2.10	2.85	2.50	1.73	2.07	not estimated

The coke did not appear to cake at all until a temperature of 800° had been reached; it swelled very little.

TABLE III.

*Percentage Composition of Gas Evolved at Different Temperatures.  
Calculated as "nitrogen-free" gas.*

	Distillation temperature.						
	500°	600	700	800	900	1000	1100
NH <sub>3</sub> .....	3.10	—	0.80	0.60	0.30	0.20	0.10
C <sub>6</sub> H <sub>6</sub> .....	3.70	1.95	1.40	0.75	0.60	0.70	0.45
H <sub>2</sub> S.....	—	—	0.20	0.35	0.30	0.25	0.25
CO.....	6.85	2.85	1.60	1.40	1.35	1.00	0.20
C <sub>2</sub> H <sub>2</sub> .....	0.95	0.20	0.10	nil	nil	nil	nil
C <sub>3</sub> H <sub>4</sub> .....	0.70	0.90	0.80	nil	0.40	0.25	0.35
CO.....	4.60	3.95	3.85	6.30	9.30	10.20	11.10
H <sub>2</sub> .....	15.70	38.75	43.30	59.65	65.50	69.90	72.90
CH <sub>4</sub> .....	51.50	48.50	45.90	28.35	20.65	14.45	12.85
C <sub>2</sub> H <sub>4</sub> .....	13.70	4.65	2.05	2.50	1.60	2.95	1.80

TABLE IV.

*Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at Different Temperatures, and Volumes of Principal Constituents.*

	Distillation temperature.					
	500°	600	700	800	900	1000 1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas ...	13.00	56.00	94.00	193.00	248.00	288.00 333.00
H <sub>2</sub> .....	2.05	20.60	40.70	116.20	162.50	201.30 242.70
CH <sub>4</sub> .....	8.45	27.30	43.20	54.70	51.20	41.60 42.80
C <sub>2</sub> H <sub>6</sub> .....	1.80	2.60	2.00	4.80	4.00	8.50 6.00
CO .....	0.60	2.20	3.60	12.20	23.10	29.40 36.90

*Coal B (Anthracite).*

Coal from Pontyberen, South Wales. The pulverised nut coal, after passing through a 240-mesh sieve, had the following ultimate analysis:

Carbon .....	92.66	} Per cent. of ash-free, dry coal
Hydrogen .....	3.14	
Oxygen .....	2.20	
Nitrogen .....	0.99	
Sulphur .....	1.01	

and it contained 3.9 per cent. of ash.

TABLE I.

*Rate of Evolution of Gas at Different Temperatures.*

Total gas from 2 grams of coal; measured at atmospheric temperature and pressure.

	Distillation temperature.				
	700°	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.
During 1st minute .....	—	50	120	250	375
" 2nd " .....	—	25	95	100	75
" 3rd " .....	—	25	40	25	15
" 4th " .....	—	20	30	20	10
" 5th " .....	—	20	15	10	10
Total first 5 minutes...	15	140	300	405	485
Next 5 minutes.....	40	50	43	40	15
" 5 " .....	—	20	10	15	10
" 15 " .....	20	30	20	5	25
" 30 " .....	5	10	5	5	15

With a distillation temperature of 600°, 50 c.c. were evolved during two hours.

FIG. 4.  
COALS D AND B.

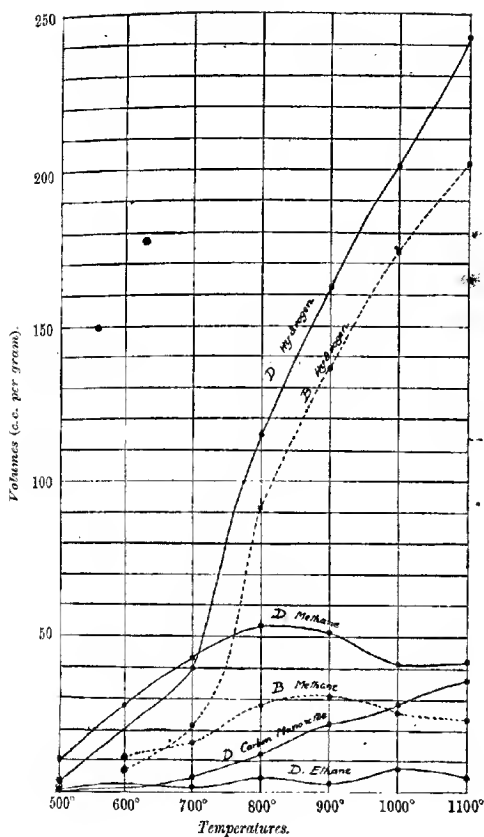


TABLE II.  
*Volatile Constituents Evolved at Different Temperatures.*

Per cent. ash-free, dry coal.

	Distillation temperature.					
	600°	700	800	900	1000	1100
Total volatile matter .....	3.57	3.76	6.18	7.82	8.77	12.50
Tarry matter .....	0.22	0.40	0.95	0.80	0.22	not estimate

There was no change in the appearance of the coal after heating except at 1100°, at which temperature some of the particles appeared to have caked slightly.

FIG. 5.

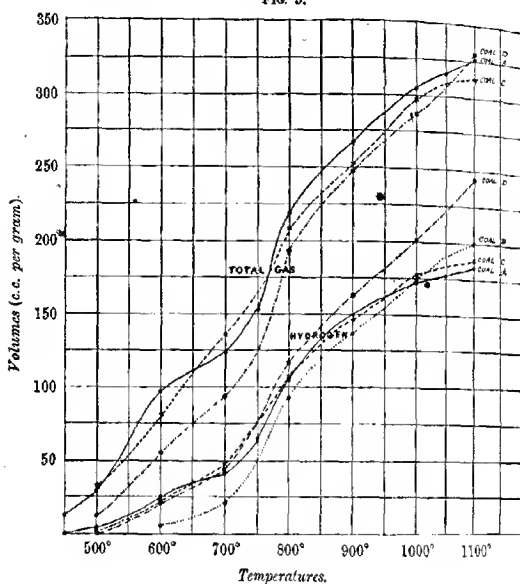


TABLE III.

Percentage Composition of Gas Evolved at Different Temperatures.  
Calculated as "nitrogen-free" gas.

	Distillation temperature.					
	600°	700	800	900	1000	1100
NH <sub>3</sub> .....	4.35	—	—	—	—	nil
C <sub>2</sub> H <sub>6</sub> .....	1.20	2.45	1.35	1.35	1.55	0.75
CO <sub>2</sub> .....	5.55	3.45	1.35	1.55	0.25	1.45
C <sub>2</sub> H <sub>2</sub> .....	nil	nil	nil	nil	nil	0.10
C <sub>2</sub> H <sub>4</sub> .....	0.10	0.20	nil	0.25	0.25	nil
CO .....	6.65	7.85	6.70	9.35	9.70	14.60
H <sub>2</sub> .....	29.35	47.30	68.65	70.50	75.35	74.10
CH <sub>4</sub> .....	51.70	36.60	21.05	15.95	11.10	8.65
C <sub>2</sub> H <sub>6</sub> .....	1.00	2.05	0.90	1.05	1.50	0.15

TABLE IV.

*Total Volume of Gas Evolved per Gram of Ash-free, Dry Coal at Different Temperatures, and Volumes of Principal Constituents.*

	Distillation temperature.					
	600°	700	800	900	1000	1100
	c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
Total gas .....	20.5	44.0	133.0	193.0	230.0	272.0
H <sub>2</sub> .....	6.0	20.8	91.3	136.0	173.5	201.5
CH <sub>4</sub> .....	10.6	16.1	28.0	30.8	25.2	24.1
C <sub>2</sub> H <sub>6</sub> .....	0.2	0.9	1.2	2.0	3.4	0.4
CO .....	1.3	3.5	8.9	18.0	22.3	39.8

These two anthracitic coals, D and B, serve to show the difference in behaviour from the bituminous as regards the gases evolved at distillation temperatures above 700°.

There is the same abrupt increase in the quantity of hydrogen evolved between 700° and 800° (Fig. 4), but the rate of increase is maintained up to the highest temperature employed, namely, 1100°, whereas, in the case of bituminous coals, as exemplified by coals A and C, the rate of increase falls off above 900° (Fig. 5).

In the case of coal D (semi-bituminous), the total quantity of gas evolved by distillation at 1100° is greater than in the case of the two bituminous coals, although at 700° it is less. The first products of distillation of the anthracitic coals are probably not such as will allow of the recombination to any great extent of free unsaturated residues to form more complex molecules, as appears to be the case with bituminous coals yielding greater quantities of gassy matter.

ALTOFFS.

### CCV.—*The Viscosity of Certain Amides.*

By ALBERT ERNEST DUNSTAN and ALBERT GEORGE MUSSELL.

The peculiarly constitutive nature of viscosity confers on it considerable value in discriminating between two possible types of structure. The amides may react as though they possessed the formula  $R \cdot CO \cdot NH_2$  or  $R \cdot C \begin{smallmatrix} OH \\ \diagup \\ NH \end{smallmatrix}$  (Tafel and Enoch, *Ber.*, 1890, 3, 1350; Lander, *Trans.*, 1903, 83, 418), although by comparison with a genuinely hydroxyimino compound, such as glycollimino-drin, Hantzsch and Voegelen (*Ber.*, 1901, 34, 3142) regard  $R \cdot CO \cdot NH_2$  as the correct formulation for the amides. From a physical point of view the amides are undoubtedly associated

(Auwers, *Zeitsch. physikal. Chem.*, 1893, **12**, 689; 1894, **15**, 33; 1897, **23**, 449; 1899, **30**, 521), and the fact that they form additive compounds (Titherley, *Trans.*, 1901, **70**, 413) indicates that the group  $\cdot\text{CO}\cdot\text{NH}_2$  possesses considerable residual affinity. In further support of the usual amidic structure may be cited the work of Hantzsch and Dollfus (*Ber.*, 1902, **35**, 226) and Schmidt (*Ber.*, 1903, **36**, 2459). Fawsitt (*Proc. Roy. Soc. Edin.*, 1904, **25**, 1, 51) found that the fatty amides in aqueous solution were non-electrolytic, and gave normal depression of the freezing point. The same chemist (*Electrochemist and Metallurgist*, 1904, **3**, 664) determined the viscosities of a few amides in aqueous solution, and showed that the viscosity increased with increasing molecular weight.

Meldrum and Turner (*Trans.*, 1908, **93**, 876), in an ebullioscopic examination of a considerable number of amides, found that 90 per cent. of those used were associated in benzene, 80 per cent. in ether, 80 per cent. in chloroform, 10 per cent. in acetone, 45 per cent. in water, and probably 20 per cent. in ethyl alcohol. They connected these results with the dielectric constants of the solvents, and considered that the carbonyl group or the nitrogen atom was the centre of association.

Turner and Merry (*Proc.*, 1910, **26**, 128), using Ramsay and Shields' method, state that all the amides investigated by them are associated.

The object of the present work was to investigate the viscosity of the amides with the view of detecting any hydroxylic nature, for such structure has been found to affect very materially this property in aqueous solution. Again, if the amides possessed the  $\cdot\text{C}\begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NE} \end{smallmatrix}$  group, then, in pyridine solution, salt formation would probably occur, with enhanced viscosity. Further, the viscosity of the amides in the free condition had not been previously investigated, and it was of interest to determine the equivalent viscosity as being likely to throw light on their relative degrees of association.

#### EXPERIMENTAL.

The viscosity of a large number of amides, both fatty and aromatic, has been determined for the free substances and for aqueous and pyridine solutions. The materials used were as follows:

*Carbamide*.—Kahlbaum's purest, m. p.  $132^\circ$ .

*Formamide*.—Kahlbaum's, redistilled under diminished pressure. 2916 grams, boiled with alcoholic potash (70 c.c. of 1.155*N*), used, after boiling, 16.25 c.c. of *N*-sulphuric acid, whence  $\text{HCO}\cdot\text{NH}_2 = 99.7$  per cent. Boiled with decomposition at  $204^\circ/758$  mm. ( $208^\circ$  corr.); b. p.  $141^\circ/65$  mm.,  $136^\circ/50$  mm. Brühl

(*Zeitsch. physikal. Chem.*, 1894, 16, 214) gives b. p. 111–112°/14 mm.

*Acetamide*.—Kahlbaum's, m. p. 82°, redistilled h. p. 215.5°/749 mm.

*Propionamide*.—Kahlbaum's, m. p. 80–81°.

*n-Butyramide*.—Kahlbaum's, m. p. 116°.

*Thiocarbamide*.—Schuchardt's, m. p. 149°, crystallised from water.

*Acetanilide*.—Prepared from aniline, recrystallised several times from water, m. p. 112°, b. p. 283°.

*Benzamide*.—Kahlbaum's, recrystallised from hot water, m. p. 128°.

*Benzanilide*.—Schuchardt's, m. p. 160°, crystallised from alcohol.

*Thiocarbanilide*.—Schuchardt's, recrystallised twice from alcohol, m. p. 153°.

*Methylacetanilide*.—Prepared from methylaniline, recrystallised from alcohol, m. p. 101°, b. p. 237°.

*Diphenylcarbanilide* (carbanilide).—Prepared from ketobenzoxazole and aniline, crystallised from much alcohol, m. p. 234° (in sealed tube).

*Urethane*.—Kahlbaum's, m. p. 51°, b. p. 179°/749 mm.

*Cyanuric Acid*.—Kahlbaum's, recrystallised from hot water.

*Formamide*.—Schuchardt's, recrystallised from hot aqueous alcohol, m. p. 46–47°, h. p. 271°.

*Phthalanil*.—Schuchardt's, m. p. 205°.

*Phthalimide*.—Schuchardt's, recrystallised from alcohol, m. p. 230°.

*Solvents*.—Conductivity water, pyridine partly from Kahlbaum, dried over potassium hydroxide, b. p. 114–116°/742 mm. (corr.), partly from crude coal-tar pyridine fractionated with a long rod-and-disk column, b. p. 116°.

*Magnitude of Experimental Error*.—Densities were taken in Sprengel pyknometers of 2 c.c. capacity. Two determinations were made, and these usually agreed within a milligram. The density error is not greater than 0.05 per cent. Times of flow were taken until about five concordant results were obtained agreeing within one second; as an example the following may be quoted:

Butyramide, 16.88 per cent. in water.

8' 27.4"; 3' 27.4"; 3' 27.6"; 3' 27.6"; 3' 27.7"; 3' 27.6". Average = 3' 27.53".

Greatest mean error = 0.17 sec.

The viscosity error may be taken as  $\pm 0.1$  per cent.

To obtain the equivalent viscosities, two or more determinations were made at different (low) concentrations. A curve was then



drawn practically linear near the origin. By arranging the equivalent concentration so low as mol. wt./20, it was possible to interpolate from this linear portion, and so obtain a more correct value than could be observed directly.

The viscosities at high temperatures are not so accurate, since it is very difficult to secure effective thermo-regulation. An example will illustrate the method:

Temperature at start.	Temperature at end.	Time of flow.
104.8*	105.0*	5.28
105.0	103.8	5.31
104.8	104.6	5.27
105.0	105.7	5.27
Average temperature 104.8		Average 5.282

The viscosity error is probably  $\pm 0.5$  per cent.

The following tables show the results obtained; the figures in the first column representing percentages of the substance in the solvent.

TABLE I.

*Amides in Aqueous Solution at 25°.*

(1). Carbamide—			(4). Propionamide—		
	Density.	Viscosity.		Density.	Viscosity.
1.02	1.000	0.00895	1.245	0.9974	0.00919
8.13	1.018	0.00929	5.65	0.9984	0.01025
11.89	1.029	0.00969	11.71	1.000	0.01188
15.47	1.033	0.01035	22.18	1.005	0.01538
23.12	1.059	0.01088	41.48	1.011	0.02030
33.28	1.087	0.01252	70.65	1.011	0.05980
38.13	1.102	0.01348			
46.18	1.125	0.01561			
(2). Formamide—			(5). n-Butyramide—		
	Density.	Viscosity.		Density.	Viscosity.
1.70	0.9999	0.00921	1.02	0.9872	0.00808
40.22	1.054	0.01182	8.11	0.9974	0.01122
52.2	1.069	0.01283	16.88	0.9984	0.01458
75.42	1.115	0.02101	17.92	0.9987	0.01511
79.15	1.118	0.02275			
100.0	1.132	0.0331*			
		0.0326*			
(3). Acetamide—			(6). Formic acid—		
	Density.	Viscosity.		Density.	Viscosity.
0.78	0.9977	0.00880	3.05	1.004	0.00907
5.82	1.001	0.00991	27.88	1.060	0.01641
17.69	1.008	0.01232	73.85	1.161	0.01879
25.95	1.015	0.01458	100.0	1.209	0.01590
37.21	1.022	0.01875			
69.28	1.038	0.04412			

\* From two specimens from Kahlbaum.

*Amides in Pyridine Solution at 25°.*

<i>isobutyramide</i> —			<i>Propionamide</i> —		
	Density.	Viscosity.		Density.	Viscosity.
5.52	0.9949	0.01251	7.92	0.9769	0.01047
12.37	1.019	0.02019	13.66	0.9789	0.01208
			23.75	0.9817	0.01615
<i>anamide</i> —			<i>Cyanuric acid</i> —		
3.87	0.9794	0.00987	3.20	0.9874	0.01038
16.27	0.9959	0.01381			
<i>azoxime</i> —			<i>Formanilide</i> —		
5.14	0.9839	0.01055	10.32	0.9903	0.01089
12.46	0.9971	0.01331	19.14	1.004	0.01335
<i>azoxanilide</i> —			<i>Phthalanil</i> —		
5.40	0.9829	0.01027	3.55	0.9821	0.009606
9.02	0.9902	0.01121			
12.75	0.9964	0.01252	<i>Phthalimide</i> —		
<i>isocyanilide</i> —			5.05	0.9876	0.009878
7.40	0.9919	0.01159	11.93	1.006	0.01182
14.51	1.005	0.01416	<i>Formamide</i> —		
<i>ethylacetamide</i> —			7.77	0.9871	0.01064
6.59	0.9786	0.00667	11.10	0.9935	0.01150
11.2	0.9819	0.01022	17.12	1.0007	0.01365
16.44	0.9844	0.01082	<i>Acetamide</i> —		
<i>uranilide</i> —			5.65	0.9814	0.01005
5.69	0.9811	0.01045	8.51	0.9826	0.01038
7.13	0.9862	0.01079	<i>Carbamide</i> —		
<i>urethane</i> —			0.91	0.9802	0.00839
9.09	0.9832	0.01070	<i>Pyridine</i> *—		
14.26	0.9859	0.01202	100.0	0.9746	0.00884

\* Hartley, Thomas, and Applebey (Trans., 1908, 93, 544) give 0.00885.

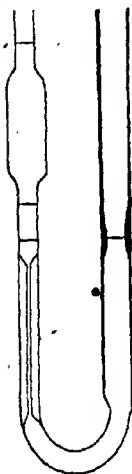
*The Viscosity of the Amides at High Temperatures.*

To obtain comparable information as to the relative state of association of the amides, it was necessary to work at somewhat elevated temperatures, seeing that propionamide melts at 81° and acetamide at 82°. A description of the apparatus used may be of interest.

A large beaker filled with cylinder oil of high flash-point was supported on wire gauze and jacketed with asbestos paper, through which two opposite longitudinal slits were cut for observations of the viscometer. Through the metal lid passed a thermometer graduated in fifths of a degree, a stirrer connected with a Henrici motor, and the viscometer. The latter was designed with the view of increased accuracy in filling. The usual method (Ostwald, *Physico-Chemical Measurements*, 1894, 163) is to run in a known

volume of liquid from a pipette. This is obviously impossible when working with a substance which is solid at the ordinary temperature, unless the pipette can be kept at a sufficiently high temperature, so that the instrument shown in Fig. 1 was used. It is of the Ostwald type, and merely possesses two etched lines at the same level on the same limb. The viscometer

FIG. 1.



is cleaned and dried, and the compound under observation is distilled into it. Where distillation is impossible, the melted substance must be filtered in. Unless filtration or distillation is resorted to, it is practically impossible to secure freedom from particles of dust, which will inevitably choke the capillary. This is the most fertile source of error in viscometry. The instrument filled just above the marks is placed in the oil-bath, and levelled by means of a gravity bob hung from the supporting clamp. After remaining for ten minutes to attain the bath temperature (a thin flame obtained from a Bunsen burner after unscrewing the chimney, and controlled by a long lever on the tap, gives excellent temperature regulation), the liquid is adjusted to the marks by a capillary pipette, and times of flow are taken and averaged. Absolute densities were measured in a 10 c.c. bottle-shaped pycnometer filled with fused compound. A correction was applied for the known coefficient of expansion of the glass, the volume being determined at

25° and 45° by the water content.

The viscometer was calibrated with ethylene dibromide in the following way:

$\text{Log viscometer constant} = \log \eta - \log \text{time} - \log \text{density.}$

At 105°,  $\eta$  for ethylene dibromide = 0.00639 (Thorpe and Rodger).

At 120°,  $\eta$  " " = 0.00562 " "

Time of flow at 105° = 77.4 secs., and at 120° = 71.9 secs.

Density at 105° = 2.009, and at 120° = 1.979.

whence  $\log K_{105} = 5.6138$ , and  $\log K_{120} = 5.5965$ .

Hence the viscosity of a compound at 120° or 105° is obtained from the equation  $\eta = K \times \text{time} \times \text{density.}$

The ethylene dibromide used for this purpose boiled at 129.5°/749 mm.

TABLE II.  
*Amides at High Temperatures.*

105°:	$\eta$ .	$d$ .	Mol. wt.	$\eta \times 10^6/M.V.$
Formamide.....	0.00748	1.061	45	181
Acetamide.....	0.0132	0.980	59	219
Propionamide.....	0.0127	0.933	73	162
Urethane.....	0.00916	1.005	89	103.5
120°:				
Formamide.....	0.00659	1.050	45	154
Acetamide.....	0.0106	0.967	59	174
Propionamide.....	0.0103	0.925	73	136
Urethane.....	0.00715	0.991	89	77.8
Formanilide.....	0.0165	1.076	121	147
Acetanilide.....	0.0222	1.034	135	170
Methylacetanilide...	0.00818	0.977	149	53.6

#### *Discussion of Results.*

##### *The Amides in Aqueous Solution.*

Formamide, acetamide, propionamide, *n*-butyramide, and carbamide were examined in aqueous solution. In Fig. 2 are plotted the viscosity-concentration curves of the above amides, together with those of formic acid and methyl alcohol for comparison.

In connexion with formamide, Walden (*Zeitsch. Electrochem.*, 1908, 14, 718) found a high value for the latent heat of fusion (50.4, acetamide being 69.4). Moreover the expression  $\frac{M\lambda\infty}{T_g^2}$  for formamide is 8.31, and for acetamide 11.51, giving the coefficients of association 1.62 formamide, and 1.17 acetamide.

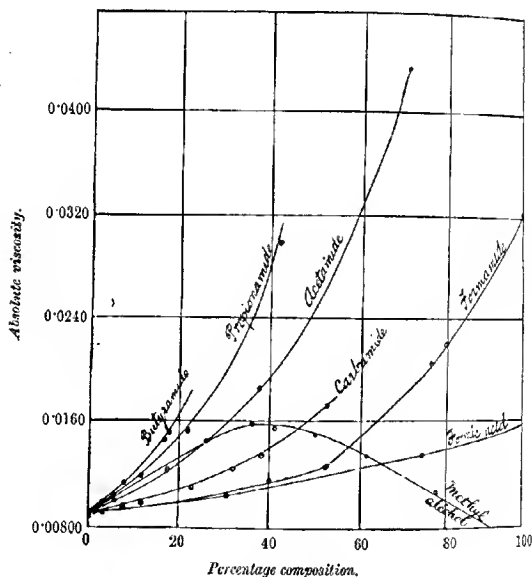
The rapid increase of viscosity with increasing amide concentration is remarkable, and indicates very considerable association on the part of these compounds. Comparing formamide and formic acid, which yield curves of similar type up to a concentration of 30 per cent., it is evident that beyond this limit the formamide curve rises steeply until the relatively high viscosity 0.0326 is reached for the pure substance.

Now it has been shown that the quantity  $\frac{\eta}{M.V.} \times 10^6$  has a series of constancy; for example, for alkyl chlorides it is 37.4, and for ketones 43.3 (Dunstan and Thole, *J. Chim. Phys.*, 1909, 7, 204). Whilst for associated compounds values in great excess of these are obtained. For formamide,  $\frac{\eta \times 10^6}{M.V.} = 682$ , and for formic acid this expression = 415. There is thus little doubt that formamide in the free state is extremely associated, and although these numbers do

not give an exact value for the degree of association, yet it is possible, qualitatively, to obtain a very fair idea of the relative extents of the molecular complexity. By measuring off the curves, the values of the viscosity coefficients at equimolecular concentrations, the following numbers are obtained:

Mol. wt.	Amide.	Equivalent viscosity at mol. wt./8 per cent.
87	Butyramide .....	122
73	Propionamide .....	110
59	Acetamide .....	102
60	Carbamide .....	94
45	Formamide .....	90
46	Formic acid .....	92
32	Methyl alcohol .....	99

FIG. 2.



The above equivalent viscosities in aqueous solution illustrate the dissociating action of the solvent. Formamide is almost completely broken down, since its equivalent viscosity is nearly identical with that of formic acid, which does not exist associated with water in aqueous solution. Methyl alcohol, on the other hand, is most probably associated with the solvent. There is a steady increase

in viscosity as the molecular weights of the amides become greater. According to Meldrum and Turner (*loc. cit.*), the amides are associated in aqueous solution with the possible exception of carbamide (formamide was not examined by them).

The position of carbamide is interesting, seeing that the curve lies almost exactly midway between those for acetamide and formamide. Although of nearly identical molecular weight, the equivalent viscosity is considerably lower than that of acetamide.

Here, however, another consideration should be advanced. Viscosity is not entirely a matter of molecular mass or molecular volume. What may be termed the molecular shape or symmetry cannot be ignored, and in accordance with this view it is found that the viscosity of *iso*-compounds differs from that of the normal isomerides. It may happen that carbamide is a more symmetrical compound than acetamide, in which case, although the degree of association might be the same, the molecular viscosity would be less.

#### *The Amides in Pyridine Solution.*

The choice of pyridine was made in the expectation that if any tendency existed towards the structure  $\text{C} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH} \end{smallmatrix}$  on the part of the amides, it would be developed by the well-known basic properties of this solvent. With the possible exceptions of thiocarbamide, cyanuric acid, and thiocarbanilide, this hope was not realised, but at the same time it will be evident from the curve that an approximate separation of the amides in the order of their molecular complexity is achieved. Pyridine is a dissociating solvent (von Laszczynski and von Gorski, *Zeitsch. Elektrochem.*, 1897, 4, 299), and, like water, tends to break up the aggregates presented to it. It is particularly noteworthy that the amide the molecular viscosity of which was smallest in the fused state, methylacetanilide, affords the curve with the least upward tendency, that is, the least effect on the viscosity of the solvent. For the sake of comparison, viscosities of the solutions have been measured at equivalent concentrations, mol. wt./20 per cent.

The order then becomes:

Mol. wt.	Amide.	At mol. wt /20 per cent.	Mol. wt.	Amide.	At mol. wt/20 per cent.
45	Formamide .....	0.0093	121	Benzamide .....	0.0108
59	Acetamide .....	0.0095	135	Acetanilide .....	0.0108
149	Methylacetanilide .	0.0097	76	Thiocarbamide.....	0.0109
89	Urethane .....	0.0097	212	Carbanilide .....	0.0110
73	Propionamide .....	0.0097	223	Phthalanil .....	0.0114
121	Formanilide.....	0.0098	197	Benzanilide .....	0.0116
60	Carbamide .....	0.0101	129	Cyanuric acid .....	0.0120
123	Phthalimide.....	0.0102	228	Thiocarbanilide ...	0.0130

The value for carbamide is not of the same order of accuracy as the other amides, seeing that a concentration of 1 per cent. was the highest obtained. If it be granted that the amides in certain instances do react as acids, then the high molecular viscosities of thiocarbamilide and benzanilide would be explained, and this explanation is at least a possible one. But at the same time the non-acidic nature of the fatty amides is emphasised. The values in pyridine solution are complicated therefore by two causes: (1) the dissociation more or less complete suffered by the dissolved substance; (2) the effect of any acidic nature of the solute. When the equivalent viscosities in pyridine are compared with those in aqueous solution, it is again noticed that formamide has the lowest value; this, of course, may be in each case due to the fact that it is the most easily dissociated, but it must be emphasised once more that the question of molecular symmetry cannot be ignored in drawing comparisons based on viscosity determinations. We intend extending this research to the investigation of the general question of solutions in the amides, and particularly to the question of relative viscosities at corresponding temperatures.

In conclusion, we desire to express our gratitude to Mr. W. E. S. Turner for many useful suggestions and criticism, and to the Research Fund of the Chemical Society for a grant in aid of the work.

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## CCVI.—The Constituents of *Leptandra*.

By FREDERICK BELDING POWER and HAROLD ROGERSON.

UNDER the title of "*leptandra*," the Pharmacopœia of the United States recognises the dried rhizome and roots of *Veronica virginica*, Linné (*Leptandra virginica*, Nuttall), a plant which is indigenous to the greater part of North America. The above-mentioned underground portion of the plant is used medicinally, and the crude resinous material obtained therefrom is one of the products to which the name "*leptandrin*" has been assigned.

The first chemical examination of "*leptandra*" appears to have been that recorded by E. S. Wayne (*Proc. Amer. Pharm. Assoc.*, 1856, p. 34), who stated that, besides essential oil, bitter extractive, tannin, gum, and resin, it contains a crystalline, bitter substance,

which separated from the ethereal solution in needles. This substance, although not further characterised, was considered to represent the active principle of the drug, and for it the name "leptandrin" has since been proposed. The same investigator (*Amer. J. Pharm.*, 1859, 31, 557) also observed the presence of "a saccharine principle having the properties of mannite." It was subsequently indicated by F. F. Mayer (*Amer. J. Pharm.*, 1863, 35, 298), and more recently by J. U. Lloyd (*Proc. Amer. Pharm. Assoc.*, 1880, 28, 421), that the bitter principle of the drug is a glucoside, although no definite substance of this class had actually been isolated. Steinmann (*Amer. J. Pharm.*, 1887, 59, 229) states that he obtained the bitter principle in crystals of a pale lemon-yellow colour, but they yielded no dextrose when boiled with dilute sulphuric acid, and their solution gave no precipitate with the usual alkaloid reagents.

It will be apparent from the brief review of the literature given above that, with the exception of the recorded presence of mannitol, nothing of a very definite nature has up to the present been known respecting the constituents of "leptandra." It was therefore deemed of interest to subject it to a complete examination, and the results are embodied in the present communication.

#### EXPERIMENTAL.

The material employed for this investigation consisted of a good quality of commercial "leptandra," which conformed in its characters to the description given of the latter in the United States Pharmacopœia.

A small portion (10 grams) of the material was first tested for an alkaloid, but the reactions were so slight as to indicate the presence of not more than traces of such a substance.

Twenty grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°)	extracted	0.11 gram	=	0.55 per cent.
Ether	"	0.56 "	=	2.80 "
Chloroform	"	1.00 "	=	5.00 "
Ethyl acetate	"	0.65 "	=	3.25 "
Alcohol	"	2.95 "	=	14.75 "

Total 5.27 grams = 26.35 per cent.

For the purpose of a complete examination, a quantity (55.56 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 19.79 kilograms.



*Distillation of the Extract with Steam. Separation of an Essential Oil.*

A quantity (2 kilograms) of the above-mentioned extract was mixed with water, and steam passed through the mixture for several hours. The distillate, which amounted to about 6 litres, contained some oily drops floating on the surface. It was thoroughly extracted with ether, the ethereal liquid being dried and the solvent removed, when 0.9 gram of an essential oil was obtained. The yield of the latter was thus equivalent to 0.16 per cent. of the weight of the drug. This essential oil, when distilled under diminished pressure, passed over between 120° and 160°/25 mm. It was a dark brown, mobile liquid, possessing a strong, persistent odour, and gave no coloration with ferric chloride.

*Non-volatile Constituents of the Extract.*

After the distillation of the extract with steam, as above described, there remained in the distillation flask a dark-coloured, aqueous liquid (A), and a quantity of a dark brown resin (B). These products, when cold, were separated by filtration, and the resin repeatedly washed with hot water until nothing further was removed, the washings being added to the aqueous liquid.

*Examination of the Aqueous Liquid (A).*

*Isolation of 3:4-Dimethoxycinnamic Acid,  
 $C_6H_3(OMe)_2 \cdot CH:CH \cdot CO_2H$ .*

The aqueous liquid was repeatedly extracted with ether, and the combined ethereal extracts evaporated to a small volume. On cooling, a quantity (5.0 grams) of a crystalline substance separated. This was removed by filtration, dried, and recrystallised from water, when it separated in yellow needles, melting at about 170°, but after repeated crystallisation from absolute alcohol it was obtained in large, colourless needles, melting at 180—181°. (Found, C=63.4; H=5.9; OMe=29.2. Calc., C=63.5; H=5.8; OMe=29.8 per cent.)

The substance was found to be an acid, and is seen to agree in its characters and composition with 3:4-dimethoxycinnamic acid,  $C_6H_3(OMe)_2 \cdot CH:CH \cdot CO_2H$ . When mixed with a portion of the latter, as obtained by the methylation of ferulic acid (Trans., 1907, 91, 893), the melting point was unchanged. Further confirmation of the identity of the acid was obtained by the preparation of its methyl ester, which separated from absolute alcohol in small prisms, melting at 64°. So far as known to us, this is the first

instance in which 3:4-dimethoxycinnamic acid has been observed to occur in nature.

The ethereal liquid from which the above-described acid had been separated was diluted somewhat, and then shaken with successive portions of aqueous ammonium carbonate. On acidifying the alkaline liquids, a solid substance was precipitated, which was likewise found to consist of 3:4-dimethoxycinnamic acid. The total amount of this acid obtained from 2 kilograms of the original alcoholic extract was 12.0 grams, and was thus equivalent to about 0.2 per cent. of the weight of the drug.

The ethereal liquid was subsequently shaken with a solution of sodium carbonate, which, however, removed nothing. It was then treated with a 10 per cent. solution of sodium hydroxide, when a quantity of resinous material was removed, but from which nothing definite could be isolated. On finally evaporating the ether, only a small amount of a yellow, amorphous product was obtained.

The original aqueous liquid (A), which had been extracted with ether as above described, was thoroughly shaken with successive portions of amyl alcohol. These liquids were then united, washed repeatedly with water, and concentrated under diminished pressure to a small volume, when, on cooling, a considerable quantity of a light brown, amorphous product separated. After removing the amyl alcohol as completely as possible, the entire amount of this product was dissolved in alcohol, and the solution poured into a large volume of water. The precipitate thus produced was collected, washed, and dried, when it could be reduced to a brown powder, but all attempts to obtain it in a crystalline state were unsuccessful. It amounted to 90 grams, or 1.6 per cent. of the weight of drug employed.

The above-described product possessed an intensely bitter and nauseous taste. It was readily soluble in alcohol, but very sparingly in water, even on boiling. Although the very dilute aqueous solution frothed strongly on agitation, the substance appeared to possess otherwise none of the characters of the saponins, and it was not sternutatory.

In order to obtain some further information respecting the character of the above-described product, a quantity (10 grams) of it was heated with 1000 c.c. of 2 per cent. aqueous sulphuric acid for about four hours, when, on cooling, a hard, black, resinous mass separated. The liquid was then distilled in a current of steam, the distillate extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On acidifying the alkaline liquid, again extracting with ether, and removing the solvent, a

small amount of an acid was obtained, which, on crystallising from water, separated in leaflets, melting at  $131-133^{\circ}$ . This acid yielded benzaldehyde on oxidation, and was identified as cinnamic acid. The ethereal liquid which had been extracted with alkali was finally evaporated, but it yielded only a trace of a deep yellow oil.

The aqueous, acid liquid remaining after the distillation with steam, as above described, was separated from the hard, black, resinous mass, which weighed 5.5 grams, and shaken with ether, the ethereal liquid being subsequently extracted with a solution of ammonium carbonate. On acidifying the alkaline liquid, again extracting with ether, and removing the solvent, about 0.3 gram of a crystalline product was obtained, which was found to consist of a mixture of acids. The ethereal liquid which had been extracted with alkali was finally evaporated, but it yielded only a small amount of a yellow oil, which gave a green coloration with ferric chloride.

After extracting the above-mentioned aqueous, acid liquid with ether, it was treated with barium hydroxide for the removal of the sulphuric acid. The filtered liquid readily reduced Fehling's solution, but no crystalline osazone could be prepared from it.

From the above results it was evident that the bitter, amorphous product, which had been obtained by extracting the original aqueous liquid with amyl alcohol, was of a complex nature, and that not more than a small proportion of it could have been glucosidic. It was, moreover, apparent that the acids which it yielded by treatment with dilute sulphuric acid were present in the form of esters, inasmuch as on heating the product with aqueous sodium hydroxide a similar mixture of acids was obtained, and in better yield. This mixture of acids was found on examination to consist chiefly of *p*-methoxycinnamic acid, together with smaller amounts of cinnamic acid and another compound which could not be identified.

The original aqueous liquid, after being extracted with amyl alcohol as above described, was concentrated somewhat, and treated with a slight excess of a solution of basic lead acetate. A copious brown precipitate was thus produced, which was collected, well washed with water, then suspended in water, decomposed by hydrogen sulphide, and the mixture filtered. The filtrate, when concentrated, was dark reddish-brown, and appeared to contain only tannic and colouring matter.

The liquid from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the lead, and the filtered liquid concentrated to a small hulk. To the syrup thus obtained

a large volume of alcohol was added, when a quantity of a crystalline substance was deposited, which was collected, washed with a little alcohol, and dried. The liquid from which this crystalline substance had been separated was deprived of alcohol, and evaporated to the consistency of a syrup. It evidently contained a large amount of a sugar, since it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 209—211°.

#### *Isolation of d-Mannitol.*

The crystalline substance above described, which amounted to 120 grams, or 2.14 per cent. of the weight of the drug, was recrystallised from alcohol, when it separated in needles, melting at 165—166°, and proved to be *d*-mannitol. (Found, C=39.6; H=7.7 per cent.)

Further confirmation of the identity of the above-described substance with mannitol was obtained by the formation of its acetyl and benzoyl derivatives.

On heating a little of the substance with acetic anhydride, a product was obtained which, when crystallised from absolute alcohol, separated in octahedra, melting at 122—124°, and consisted of the hexa-*a* styl derivative of mannitol.

Another portion of the substance was benzoylated by the Schotten-Baumann method, as employed by Panormoff (*J. Russ. Phys. Chem. Soc.*, 1891, 23, 375), when a product was obtained which was soluble in chloroform, but, on the removal of the solvent, formed a syrup. On dissolving this, however, in a small volume of ether, it yielded a mass of needle-shaped crystals, which melted at 149°, and after recrystallisation from a mixture of ethyl acetate and alcohol, or from acetic anhydride, the melting point remained unchanged. (Found, C=71.3; H=4.9. Calc., C=71.4; H=4.7 per cent.)

This substance is thus seen to be hexabenzoylmannitol,  $C_6H_5O_6(CO \cdot C_6H_5)_6$ , the melting point of which has been given as 149° by Skraup (*Monatsh.*, 1889, 10, 389) and by Panormoff (*loc. cit.*), but was incorrectly recorded by Stohmann, Rodatz, and Herzberg (*J. pr. Chem.*, 1887, [ii], 36, 354) as 124—125°.

The optical rotatory power of hexabenzoylmannitol does not appear to have previously been recorded, and this was therefore determined, with the following result:

0.4238, made up to 20 c.c. with chloroform, gave  $\alpha_D + 2.9'$  in a 2-dm. tube, whence  $[\alpha]_D + 50.7^\circ$ .

If the benzoylation of mannitol is conducted in the usual manner, by adding the benzoyl chloride in small quantities at a time, a dibenzoyl derivative,  $C_6H_{12}O_6(CO \cdot C_6H_5)_2$ , is obtained. This is very

sparingly soluble in the usual organic solvents, and crystallises in small, prismatic needles, which melt at 178—180°. (Found, C=61.0; H=5.8. Calc., C=61.5; H=5.6 per cent.)

0.3410, made up to 20 c.c. with pyridine, gave  $\alpha_D + 0^\circ 22'$  in a 2-dm. tube, whence  $[\alpha]_D + 10.7^\circ$ .

Dihenzoylmannitol has previously been obtained by Einhorn and Hollandt (*Annalen*, 1898, 301, 102), who recorded its melting point as 178°. On adding an excess of benzoyl chloride to a hot solution of mannitol in pyridine, according to the method of the last-mentioned investigators, a crystalline substance began to separate at once, which was evidently the dihenzoyl derivative. When, however, the liquid was heated a little longer, a vigorous reaction ensued, which soon subsided, and a perfectly clear solution was obtained. The product was then poured into water and extracted with ether, when a substance was obtained which melted at 149°, and proved to be hexabenzoylmannitol.

#### *Examination of the Resin (B).*

This was a dark brown, brittle mass, and amounted to about 350 grams, being thus equivalent to 6.2 per cent. of the drug. It was dissolved in alcohol, mixed with purified sawdust, and the mixture successively extracted in a Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

#### *Petroleum Extract of the Resin.*

This was a dark brown mass, amounting to 24.5 grams. The extract was dissolved in ether, and the ethereal solution shaken with aqueous ammonium carbonate, which, however, removed only a small amount of resinous material, together with a trace of 3:4-dimethoxycinnamic acid. The ethereal solution was then shaken with aqueous potassium carbonate, and the alkaline liquid acidified, when a quantity of black, tarry material was precipitated. This was distilled several times under diminished pressure, when a product was finally obtained which passed over between 220° and 240°/15 mm. as a light yellow oil, and partly solidified on cooling. The free acids thus obtained amounted to 3.7 grams, and were examined together with the combined acids which will subsequently be described.

After treatment with potassium carbonate, as above described, the ethereal solution was shaken with aqueous potassium hydroxide, which, however, removed nothing. On finally evaporating the ether, a residue was obtained, which was hydrolysed by heating with an alcoholic solution of potassium hydroxide. The alcohol was then

removed, and the cooled, aqueous, alkaline liquid extracted with ether, the ethereal liquid being dried and the solvent evaporated. On dissolving the residue in alcohol, a small quantity of a solid separated, which, when recrystallised from ethyl acetate, melted at 62–65°, and was found to consist of a hydrocarbon and an alcohol, but the amount was too small to permit of their separation.

*Isolation of a Phytosterol, Verosterol,  $C_{27}H_{46}O, H_2O$ .*

The alcoholic filtrate from the above-mentioned solid was concentrated to a small bulk, when, after two or three days, a quantity of a crystalline substance separated. This was collected, washed, and recrystallised from a mixture of ethyl acetate and dilute alcohol, when it separated in flat needles, melting at 135–136°, and gave the colour reactions of the phytosterols:

0.2500, on heating at 110°, lost 0.0126  $H_2O$ .  $H_2O=5.0$ .

0.1230 \* gave 0.3764  $CO_2$  and 0.1360  $H_2O$ .  $C=83.5$ ;  $H=12.3$ .

$C_{27}H_{46}O, H_2O$  requires  $H_2O=4.5$  per cent.

$C_{27}H_{46}O$  requires  $C=83.9$ ;  $H=11.9$  per cent.

A determination of its optical rotatory power gave the following result:

0.2374,\* made up to 20 c.c. with chloroform, gave  $\alpha_D -0.47'$  in a 2-dm. tube, whence  $[\alpha]_D -33.0^\circ$ .

A small amount of the phytosterol was converted into its acetate, which separated from acetic anhydride in flat needles, melting at 119–120°.

The above-described phytosterol evidently represents a member of this class of substances which is widely distributed in nature, and compounds possessing practically the same physical characters have previously been obtained in these laboratories from various sources, such as olive bark, wild cherry bark, and jalap (Trans., 1908, 93, 909; 1909, 95, 246; *J. Amer. Chem. Soc.*, 1910, 32, 87; compare also Menozzi and Moreschi, *Atti R. Accad. Lincei*, 1910, [v], 19, i, 187). In view of these facts, and in order to distinguish the above-described phytosterol from sitosterol, which differs by the higher melting point of its acetate (*Monatsh.*, 1897, 18, 551), it would appear desirable to assign to it a specific name. It is therefore proposed to designate it *verosterol*, with reference to the generic name of the plant, *Veronica*, from which it has now been obtained.

*Identification of the Fatty Acids.*

The alkaline liquid, which had been extracted with ether as above described, was acidified, and the liberated fatty acids collected,

\* Anhydrous substance.

dried, and distilled under diminished pressure, when they passed over between  $220^{\circ}$  and  $250^{\circ}/15$  mm. as a pale yellow oil. The acids thus obtained, which amounted to 4.2 grams, were mixed with the previously mentioned portion of acids present in the free state, and the whole converted into their lead salts, the latter being then digested with ether, when a portion was dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 4.2 grams of liquid acids, whilst the insoluble portion gave 3.3 grams of solid acids.

*The Liquid Acids.*—These acids, when distilled under diminished pressure, passed over between  $215^{\circ}$  and  $235^{\circ}/15$  mm. as a yellow oil. An analysis and a determination of the constants gave the following results:

0.1738 gave 0.4842  $\text{CO}_2$  and 0.1788  $\text{H}_2\text{O}$ .  $\text{C}=76.0$ ;  $\text{H}=11.4$ .

0.3788 absorbed 0.4872 iodine. Iodine value=128.6.

0.1540 neutralised 0.0307  $\text{KOH}$ . Neutralisation value=199.3.

$\text{C}_{13}\text{H}_{24}\text{O}_2$  requires  $\text{C}=76.6$ ;  $\text{H}=12.1$  per cent. Iodine value=90.1;  
Neutralisation value=198.9.

$\text{C}_{15}\text{H}_{22}\text{O}_2$  requires  $\text{C}=77.1$ ;  $\text{H}=11.4$  per cent. Iodine value=181.4;  
Neutralisation value=200.4.

It is evident from the above results that the liquid acids consisted of a mixture of oleic and linolic acids.

*The Solid Acids.*—These acids, after being again distilled under diminished pressure, were crystallised twice from ethyl acetate, when they melted at  $54-56^{\circ}$ :

0.1512 gave 0.4190  $\text{CO}_2$  and 0.1728  $\text{H}_2\text{O}$ .  $\text{C}=75.6$ ;  $\text{H}=12.7$ .

0.2864 neutralised 0.0590  $\text{KOH}$ . Neutralisation value=206.

$\text{C}_{16}\text{H}_{32}\text{O}_2$  requires  $\text{C}=75.0$ ;  $\text{H}=12.5$  per cent.

Neutralisation value=219.1.

$\text{C}_{18}\text{H}_{36}\text{O}_2$  requires  $\text{C}=76.1$ ;  $\text{H}=12.7$  per cent.

Neutralisation value=197.5.

These results indicate that the solid acids consisted of a mixture of palmitic and stearic acids in about equal proportions.

#### *Ethereal Extract of the Resin.*

During the extraction of the resin with ether a quantity of a sparingly soluble, yellowish-brown substance was deposited, and when the extraction was complete this was collected, washed with ether, and dried, when it was found to weigh 5 grams. It was entirely amorphous, and proved to be similar in character to the product extracted from the original aqueous liquid by amyl alcohol,

which has already been described. On heating with aqueous sodium hydroxide, it yielded *p*-methoxycinnamic acid, which was subsequently obtained in larger amount from the chloroform extract of the resin.

The portion of extract, which was more readily soluble in ether consisted of a dark resinous mass, amounting to 95 grams. It was thoroughly examined, but nothing except a small quantity of 3:4 dimethoxycinnamic acid could be isolated from it.

#### *Chloroform Extract of the Resin.*

This was a dark-coloured resinous mass, weighing 135 grams. It could easily be reduced to a fine powder, which was tasteless. The chloroform solution of the resin was shaken with aqueous ammonium carbonate, when a small quantity of 3:4-dimethoxycinnamic acid was removed. The liquid was then shaken with a solution of sodium carbonate, but only a small amount of a resinous product was obtained.

#### *Isolation of p-Methoxycinnamic Acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ .*

After treating the chloroform liquid with the alkaline carbonates, as above described, it was shaken with successive portions of a 10 per cent. solution of sodium hydroxide. These liquids were united and acidified, when a large quantity of a black, resinous product was precipitated. This resinous product was then treated with chloroform, in which it only partly dissolved. The chloroform solution was shaken with aqueous sodium carbonate, and the alkaline liquid acidified, when a crystalline precipitate was obtained. It was thus evident that on shaking the original chloroform liquid with alkali hydroxide, some constituent of it had been hydrolysed. The crystalline precipitate was collected, washed, and dried, when it amounted to 14 grams. By fractional crystallisation from ethyl acetate, it was found to consist of a mixture of 3:4-dimethoxycinnamic acid and an acid which separated in iridescent, prismatic needles. The latter melted at  $170^\circ$ , assuming a "liquid-crystalline" phase, which persisted until the temperature of  $181\text{--}182^\circ$  was reached, when it passed into the ordinary liquid state. The "crystalline" character of the liquid between  $170^\circ$  and  $181^\circ$  was confirmed by observing it through crossed Nicol's prisms. The last-mentioned acid was analysed. (Found,  $\text{C}=67.3$ ;  $\text{H}=5.8$ ;  $\text{OMe}=17.3$ . Calc.,  $\text{C}=67.4$ ;  $\text{H}=5.6$ ;  $\text{OMe}=17.4$  per cent.)

In order further to characterise this acid, its methyl ester was prepared. This was accomplished by boiling a solution of the acid in methyl alcohol with a few drops of concentrated sulphuric acid



for about two hours on the water-bath. The product so obtained was recrystallised from absolute alcohol, when it separated in flat needles, melting at 88–90°.

The above results render it evident that the substance under examination was *p*-methoxycinnamic acid, which appears only once previously to have been observed to occur in nature. In the form of its ethyl ester, it was found by van Romburgh to be the chief constituent of the essential oil of *Kaempferia galanga*, Linné (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 38; 1902, **4**, 618; Schimmel's *Bericht*, Oct., 1900, p. 37, and April, 1903, p. 38).

•As it appears not to have previously been recorded that *p*-methoxycinnamic acid shows, on heating, a "liquid-crystalline" phase, it was deemed desirable to confirm this observation by means of the synthetically prepared acid. For this purpose a small quantity of *p*-coumaric acid was methylated by means of methyl sulphate, and the product recrystallised from ethyl acetate, when it separated in prismatic needles, melting to the "liquid-crystalline" phase at 170°, and then passing to the ordinary liquid state at 181–182°. A mixture of the naturally-occurring and synthetic acids likewise showed exactly the same behaviour at the same temperatures, and their identity was therefore definitely established.

The chloroform liquid from which the above acids had been isolated was finally evaporated for the removal of the solvent. A resinous product was thus obtained, from which, however, nothing crystalline could be isolated.

#### *Ethyl Acetate and Alcohol Extracts of the Resin.*

These extracts were dark, resinous products, amounting to 77.5 and 32.0 grams respectively. They were heated with a 5 per cent. solution of sulphuric acid in aqueous alcohol, but, with the exception of a small quantity of sugar yielding *d*-phenylglucosazone (m. p. 209–210°), nothing definite was obtained.

#### *Summary.*

The results of the present investigation may be summarised as follows:

The material employed was commercial "leptandra," consisting of the rhizome and roots of *Veronica virginica*, Linné (*Leptandra virginica*, Nuttall).

An alcoholic extract of this material, when distilled with steam, yielded an amount of essential oil equivalent to 0.16 per cent. of the weight of the drug. This essential oil was a dark brown liquid, which distilled between 120° and 160°/25 mm.

The portion of the extract which was soluble in water contained 3:4-dimethoxycinnamic acid, a quantity of mannitol, amounting to 2.14 per cent. of the weight of the drug, and a sugar which yielded *d*-phenylglucosazone (m. p. 209—211°), together with some tannic and colouring matter. It yielded, furthermore, a quantity of a brown, amorphous product, which possessed an intensely bitter, nauseous taste, and amounted to 1.6 per cent. of the weight of the drug. By the hydrolysis of this product there were obtained, besides resinous material, cinnamic and *p*-methoxycinnamic acids.

The portion of the extract which was insoluble in water consisted chiefly of a dark brown resin, which amounted to 6.2 per cent. of the weight of the drug. From this resin the following substances were obtained: A phytosterol,  $C_{27}H_{46}O$  (m. p. 135—136°;  $[\alpha]_D -33.0^\circ$ ), which it is proposed to designate *verosterol*; a mixture of fatty acids, consisting apparently of oleic, linolic, palmitic, and stearic acids; *p*-methoxycinnamic acid, which was present in the form of an ester; and a very small amount of 3:4-dimethoxycinnamic acid, which had probably been occluded by the resin.

It has been observed that *p*-methoxycinnamic acid, when melted, passes into a "liquid-crystalline" phase, which persists until a temperature of 181—182° is reached.

It has not been possible to confirm the statement recorded in the literature that "leptandra" contains a crystalline, bitter glucoside, designated as "leptandrin," to which its activity may be attributed. Steinmann (*Amer. J. Pharm.*, 1887, **59**, 229) obtained from "leptandra," in an amount of about 0.1 per cent., a crystalline, yellow substance, which possessed a very bitter taste, and was found not to be a glucoside, although it was not further characterised. From the method by which this substance was isolated, it appears highly probable that it consisted of 3:4-dimethoxycinnamic acid, contaminated with a little of the above-mentioned, bitter, amorphous product. The fact that an aqueous solution of this product froths strongly on agitation has doubtless led to the statement recorded in the literature that "leptandra" contains saponin.

Some tests with preparations of "leptandra," which were kindly conducted for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, led to the following conclusions.

Both the crude resin and the bitter, amorphous product obtained from the portion of the alcoholic extract which was soluble in water were administered by the mouth to dogs, in doses of 1 gram each, but without any visible effect. The bitter, amorphous product was also tested on the mammal by intravenous injection, and on the isolated mammalian heart, but no characteristic action could be

observed. Although the total alcoholic extract of the drug, when given to a dog in doses of 5 grams, produced vomiting, this may be attributed to its nauseous taste and irritant effect on the stomach, rather than to any specific action.

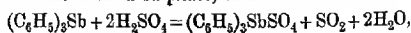
THE WELLCOME CHEMICAL RESEARCH LABORATORIES,  
LONDON, E.C.

## CCVII.—Aromatic Antimony Compounds. Part I. The Oxidation and Nitration of Triphenylstibine.

By PERCY MAY.

VARIOUS aromatic derivatives of antimony of the type  $R_3Sb$  and  $R_3SbX_2$ , in which R represents phenyl, tolyl, anisyl, etc., and X represents Cl, Br,  $NO_3$ , or OH, have been prepared by Michaelis and his pupils (Michaelis and Reese, *Annalen*, 1886, 233, 52; Michaelis and Genzken, *Annalen*, 1887, 242, 176; Löloff, *Ber.*, 1897, 30, 2834), but nevertheless far less work has been carried out with these compounds than with the corresponding derivatives of arsenic. Michaelis and Reese showed that the compound  $(C_6H_5)_3Sb(OH)_2$  is amphoteric in character, and it therefore appeared to be of interest to observe the effect of the introduction of a nitro-group on the relative stability of the various compounds, such as  $R_3SbCl_2$ ,  $R_3Sb(OH)_2$ ,  $R_3Sb(NO_3)_2$ . Michaelis and Reese prepared the compound  $(C_6H_5)_3Sb(NO_3)_2$  by the action of nitric acid on triphenylstibine, but if, at the same time, a nitro-group could be introduced into the benzene nuclei, the basicity of the compound  $R_3Sb(OH)_2$  might be so depressed that a nitrate such as  $R_3Sb(NO_3)_2$  could no longer be formed, and the resulting compound might be of the type  $R_3Sb(NO_3)(OH)$ .

On nitration, triphenylstibine yields *trinitrotriphenylstibine dihydroxide*,  $(C_6H_4NO_2)_3Sb(OH)_2$ . It does not appear to be capable of forming a stable sulphate or nitrate, but a *chloride* has been prepared, and it therefore appeared to be desirable to obtain some further information as to the relative stability of the parent substance,  $(C_6H_5)_3Sb(OH)_2$ , and its salts, and, if possible, to prepare the hitherto unknown normal sulphate,  $(C_6H_5)_3SbSO_4$ . Triphenylstibine readily reduces concentrated sulphuric acid, with the formation of the desired sulphate, thus:



and this compound could also be obtained by dissolving the corre-

sponding hydroxide in concentrated sulphuric acid. Dilute sulphuric acid does not attack triphenylstibine, but permanganate and dilute sulphuric acid oxidise it to the hydroxide,  $(C_6H_5)_3Sb(OH)_3$ . This reaction is of interest from a twofold point of view. On the one hand, it indicates that the sulphate is far less stable than the chloride,\* and, on the other hand, it affords fresh evidence of the great stability of the molecule of triphenylstibine as a whole. If alkaline permanganate be used as the oxidising agent, a better yield of the dihydroxide is obtained. Michaelis and Reese state that solutions of this substance in alkali are reprecipitated by mineral acids, but on repeating these experiments it was found that dilute nitric or sulphuric acids produced no precipitate, whilst hydrochloric acid caused precipitation even in very dilute solutions. Probably the experiments of Michaelis and Reese were confined to halogen acids. Similarly, solutions of triphenylstibine sulphate and nitrate in the corresponding concentrated acids can be diluted indefinitely, although these substances themselves are insoluble in dilute acids, but, on addition of dilute hydrochloric acid to their dilute solutions, an immediate precipitate of the chloride is obtained.

The introduction of a nitro-group into the benzene nuclei of the complex  $R_3Sb(OH)_3$  not only reduces the salt-forming power of the molecule, but also lowers its stability as a whole. This is shown by the fact that the trinitro-derivative is partly decomposed when boiled with aqueous alkali, yielding a small quantity of nitrobenzene.

#### • EXPERIMENTAL.

The triphenylstibine used in this investigation was prepared by Michaelis and Reese's method, shortened and simplified in some of its details.† The long method of purification after extraction with alcoholic hydrochloric acid, described by these authors, was omitted, the product being instead directly recrystallised from light petroleum. Pure triphenylstibine was thus obtained, the yield being 70 per cent. of the theoretical. The material contained in the petroleum mother liquor was converted into the dichloride, which, after recrystallisation, was still contaminated with traces of an impurity having an extremely irritant action on the mucous membrane. This was finally removed by dissolving the product in concentrated sulphuric acid, pouring the product into aqueous alcohol, and setting aside to crystallise.

\* Triphenylstibine hydroxide combines readily with dilute hydrochloric acid, forming the dichloride.

† A stock solution of dry antimony chloride in dry benzene, made up for these preparations, gradually acquired a deep magenta colour even in the dark.

*Nitration of Triphenylstibine and Preparation of Trinitrophenylstibine Dihydroxide,  $(C_6H_4 \cdot NO_2)_3Sb(OH)_2$ .*

Triphenylstibine was added, in small quantities at a time, to an excess of a mixture of three parts of sulphuric acid and one part of nitric acid, at about 40°. When cold, the mixture was poured into ice-water, the temperature being kept below 25°. The yellow precipitate thus obtained was recrystallised from glacial acetic acid, in which it is very soluble, and separates in flat, transparent, pale yellow crystals, melting at 190–191°. It is also soluble to some extent in alcohol or ether, but does not crystallise well from these solvents. It is insoluble in water, and almost insoluble in benzene, light petroleum, etc.:

Found, C=41.74; H=2.91; N=7.79, 7.91; Sb=22.06.

$C_{18}H_{14}O_8N_3Sb$  requires C=41.5; H=2.72; N=8.07;  
Sb=23.11 per cent.

On treatment with Devarda's alloy no ammonia is evolved. When boiled with glacial acetic acid and zinc dust, or with alcohol, hydrochloric acid, and tin, it yields an easily diazotisable amine, which was not further investigated, as work on this compound is being carried out by Morgan, Micklethwait, and Whitby (Proc., 1910, 26, 151).

*Trinitrophenylstibine Dichloride,  $(C_6H_4 \cdot NO_2)_3SbCl_2$ .*

This compound is formed, together with the hydroxy-chloride, by boiling trinitrophenylstibine dihydroxide with alcoholic hydrochloric acid. After recrystallising, the product still appeared to be impure, and analysis indicated that it was a mixture of the dichloride and the hydroxy-chloride. The pure dichloride was obtained by the direct nitration of triphenylstibine dichloride, which was dissolved in concentrated sulphuric acid, and then nitrated in the same manner as triphenylstibine. It separates from glacial acetic acid in clusters of small crystals, melting at 157°, which are readily soluble in concentrated nitric acid or glacial acetic acid. As this substance was only obtained in small amount, its properties were not further investigated.

Found, Cl=12.37.

$C_{18}H_{12}O_6N_3Cl_2Sb$  requires Cl=12.73 per cent.

*Triphenylstibine Sulphate,  $(C_6H_5)_3SbSO_4$ .*

Five grams of triphenylstibine were warmed with an excess of concentrated sulphuric acid on the water-bath. A vigorous reaction suddenly set in, sulphur dioxide being evolved, and a white pre-

precipitate formed, which was filtered on asbestos, and washed with cold alcohol, a portion being afterwards extracted with this solvent, in which it is only very sparingly soluble. Small crystals were thus obtained, and similar crystals separated on evaporation of the mother liquor after dilution with water. These crystals melt above  $300^{\circ}$ , and are soluble in concentrated sulphuric acid, very sparingly so in alcohol, and insoluble in water, dilute sulphuric acid, and most other solvents. The substance is decomposed by warming with aqueous sodium hydroxide, forming sodium sulphate and triphenylstibine hydroxide, the latter dissolving in the excess of alkali:

Found,  $S=7.30$ .

$C_{18}H_{15}O_4SSb$  requires  $S=7.17$  per cent.

A solution of the sulphate in sulphuric acid may also be obtained by dissolving triphenylstibine hydroxide in the concentrated acid, and this solution, as also the sulphuric acid mother liquor mentioned above, can be largely diluted without any precipitation occurring, but on adding a drop of hydrochloric acid to solutions of any concentration, a precipitate is formed, which, after recrystallisation from alcohol, was found to have the characteristic crystalline form and melting point of triphenylstibine dichloride.

#### *Oxidation of Triphenylstibine with Permanganate.*

(1) *In Alkaline Solution.*—Triphenylstibine was boiled for three hours with alkaline permanganate, the manganese dioxide removed, and a portion of the filtrate acidified with hydrochloric acid. A white precipitate was produced, which was recrystallised from alcohol and found to be triphenylstibine dichloride. Another portion of the filtrate was acidified with dilute sulphuric acid, and in this case no precipitate was formed. Evidently the first product of the oxidation is triphenylstibine hydroxide, which dissolves in the alkali, giving solutions from which hydrochloric acid precipitates the chloride, but which are not precipitated by sulphuric or nitric acids.

(2) *In Acid Solution.*—Five grams of triphenylstibine were warmed on the water-bath with an excess of 1 per cent. permanganate and dilute sulphuric acid. The permanganate was gradually decolorised with a slight evolution of carbon dioxide; more permanganate was added from time to time, and finally the precipitate was collected and extracted with alcohol. In this way, a small quantity of a substance was obtained which melted at  $210^{\circ}$ , contained no sulphur, and appeared to be identical with triphenylstibine hydroxide, as prepared by Michaelis and Reese. This substance was obtained by them in the form of an amorphous powder, but a modification of their method of preparation led to

its being obtained in a well-crystallised state. An alcoholic solution of triphenylstibine dichloride was added to an equal volume of 2*N*-aqueous sodium hydroxide, and the mixture set aside. After some days, triphenylstibine hydroxide crystallised out in beautiful leaflets, which were washed with water and dried. The product was then found to melt at 210°, and resembled the product obtained by Michaelis and Reese in its behaviour towards reagents.

I wish to express my thanks to Sir William Ramsay and to Professor Collic for the interest they have taken in this work, and to the Research Fund Committee of the Chemical Society for a grant towards the expenses thereof.

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LONDON.

### CCVIII.—*The Formation of Tolane Derivatives from p-Chlorotoluene and 3:4-Dichlorotoluene.*

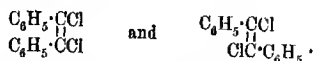
By JAMES KENNER and ERNEST WITHAM.

As is well known, the chlorination of toluene at its boiling point leads to the formation of benzotrichloride. On one occasion, however, Liebermann and Homeyer (*Ber.*, 1879, 12, 1971), and later Gattermann (*Ber.*, 1884, 17, 2601), observed the formation of a solid substance as chief product during this reaction, and identified it as tolane tetrachloride, which had previously been obtained by Zinin by the action of phosphorus pentachloride on benzil.

During the preparation of chlorobenzylidene chlorides from *p*-chlorotoluene and 3:4-dichlorotoluene, Armstrong and Wynne similarly obtained products which were identified as di- and tetrachloro-tolane tetrachlorides. The present authors have also had the same experience in preparing *p*-chlorobenzotrichloride from *p*-chlorotoluene, but, in common with earlier investigators of this reaction, they have failed to find a clue to the conditions which lead to the formation of the tolane derivative.

Liebermann and Homeyer (*loc. cit.*), it is true, attributed the condensation to sulphuric acid which had been carried over into the mixture, but in the case of the authors' experiments such an explanation is improbable, as the gas, after being passed through sulphuric acid, was led through a tube packed with asbestos, and, moreover, the introduction of sulphuric acid into the boiling *p*-chlorotoluene has not been found to initiate the condensation. This is the more unfortunate as the only other general method

of preparing tolane tetrachloride and its derivatives is that used first by Hanhart (*Ber.*, 1882, 15, 899), which consists in the removal of chlorine from benzotrichloride by the action of copper powder, and does not give satisfactory results, either as regards yield or purity of product. Hanhart, apparently unable to isolate any definite substance from the tarry product, had recourse to distillation, and obtained the two forms of tolane dichloride, now recognised as the stereoisomerides:



Onufrowicz (*Ber.*, 1884, 17, 833), who succeeded in isolating the tetrachloride, showed at the same time that it could be converted into *cis*-tolane dichloride by distillation, thus explaining Hanhart's result.

Later, Fox (*Ber.*, 1893, 26, 653), without reference to Onufrowicz's paper, carried out the same reaction with *o*-chlorobenzotrichloride, and distilled the product, obtaining the *cis*- and *trans*-2:2'-dichloro-tolane dichlorides. The authors have repeated Fox's work in the hope of separating the tetrachloride, but have been unable to find any evidence of its production, and, as recorded on p. 1966, succeeded, as he did, in isolating only the dichlorides.

As *p*-chlorobenzotrichloride, unlike the *o*-derivative, forms the tetrachloride, which can be isolated without difficulty, the opportunity was taken of testing the applicability of the decomposition observed by Onufrowicz to substituted tolane tetrachlorides. As was expected, 4:4'-dichlorotolane tetrachloride, when distilled, behaves in a precisely similar manner to tolane tetrachloride, and yields the *cis*-form of the dichloride.

Further, the tetrachloride was submitted to reduction, and results of some interest were obtained. Zinin (*Ber.*, 1871, 4, 289) showed that the action of zinc on alcoholic solutions of tolane tetrachloride led to the formation of the stereoisomeric dichlorides. Liebermann and Homeyer (*Ber.*, 1879, 12, 1971) used zinc dust in place of zinc, and obtained the same products, whilst Lachowicz (*Ber.*, 1884, 17, 1165) subsequently arrived at the same result by reducing a boiling concentrated acetic acid solution with iron filings. Wislicenus and Blank (*Annalen*, 1888, 248, 1) repeated Zinin's work, and Eiloart (*Amer. Chem. J.*, 1890, 12, 239), who studied the two dichlorides from the stereochemical point of view, upheld the opinion already expressed by Wislicenus (*loc. cit.*), that the less soluble isomeride, with the higher melting point, was the *cis*-form, although it may be remarked that this is contrary to the usual rule.



The reduction products obtained from 4: 4'-dichlorotolane tetrachloride in alcoholic solution by means of zinc dust vary according to the temperature employed. If conducted at 50°, the products are the two 4: 4'-dichlorotolane dichlorides, which respectively melt at 166—167° and 86—87°, and, in addition, 4: 4'-dichlorotolane; but if carried out at the boiling point of the alcoholic solution, the isomeride melting at 166—167° can no longer be found, the reduction products being the dichloride of lower melting point and 4: 4'-dichlorotolane.

If the conclusions drawn by Wislicenus and Blank respecting the *cis*- and *trans*-isomerism of the tolane dichlorides can be accepted, then it will follow by analogy that the dichlorotolane dichloride, melting at 166—167°, will be the *cis*-form. The entire absence of this isomeride from the reduction product obtained by working at the higher temperature, and the evidence that, unlike the dichloride (m. p. 86—87°), it is readily reduced may perhaps be regarded as supporting this view.

As already mentioned, tolane tetrachloride was originally obtained by Zinin by the action of phosphorus pentachloride on benzil, and this would doubtless provide a general method of preparation were it not that, as is well known, the isolation of the benzoin which should furnish the benzils on oxidation has been accomplished only in a few instances. Especially is this the case where negatively substituted aldehydes are submitted to the benzoin reaction. The authors hoped to use *o*-chlorobenzaldehyde as the starting point for the preparation of the 2: 2'-dichlorotolane tetrachloride, which could not be isolated in the experiments already mentioned, but found that when the benzoin condensation was attempted, *o*-chlorobenzoic acid was the chief product. Greater success attended experiments with *p*-chlorobenzaldehyde, for although the product of the benzoin condensation was a resinous mass from which the pure substance could not be isolated, oxidation with nitric acid led to the production of the 4: 4'-dichlorobenzil, identical with the substance obtained by hydrolysing 4: 4'-dichlorotolane tetrachloride with acetic acid by Liebermann and Homeyer's method.

It has not hitherto been possible to apply the reaction to the preparation of 2: 2'-dichlorobenzil, because the attempt to prepare 2: 2'-dichlorotolane tetrachloride by the chlorination of the *cis*-dichloride merely led to the conversion of the greater part into the more stable *trans*-form. Chlorine is known to be a particularly effective agent for the interconversion of stereoisomerides. Liebermann and Homeyer (*loc. cit.*) confirmed Limpricht's statement that the tolane dichlorides were stable towards acetic acid, and the

present authors found the same to hold good for the 2:2'-dichlorotolane dichlorides.

# EXPERIMENTAL.

Armstrong and Wynne (*private communication*), in the preparation of *p*-chlorobenzylidene chloride from *p*-chlorotoluene, employed chlorine prepared from manganese dioxide and hydrochloric acid, washed by passage through water, and dried over sulphuric acid. For each of seven operations, 126 grams of *p*-chlorotoluene were used, and it was found that in the first two only a very small quantity, but in the last five, considerable amounts, of 4:4'-dichlorotolane tetrachloride separated in a crystalline form on cooling. The rate at which the chlorine was absorbed did not seem to influence the tolane condensation: thus, in the first two and the last two operations the figures for increase in weight due to chlorination and, in brackets, the duration in hours were 74 (16), 71 (15), 70 (14), 67 (16)—the calculated increase in weight being 69 grams.

The present authors have used liquid chlorine obtained from Kahlbaum as the source of the gas, and have passed the chlorine through sulphuric acid (to allow of the rate being checked) and asbestos wool before introducing it into the boiling *p*-chlorotoluene. With one exception they have been unsuccessful in obtaining the 4:4'-dichlorotolane tetrachloride. Throughout, they have chlorinated to the stage of *p*-chlorobenzotrichloride, and the usual daily increase in weight was 15 grams, but on the one occasion when the tetrachloride was formed, 44 grams on the first day, and 22 on the second, were taken up. The yield of the tetrachloride from 100 grams of *p*-chlorotoluene was 44 grams, and the mother liquor consisted of *p*-chlorobenzotrichloride. All attempts to repeat the conditions leading to the formation of the tolane derivative have been unsuccessful.

4:4'-Dichlorotolane tetrachloride,  $C_6H_4Cl \cdot CCl_2 \cdot CCl_2 \cdot C_6H_4Cl$ , crystallises from chloroform in thin, well-defined, flat plates. It melts at  $190^\circ$ , and dissolves only sparingly in alcohol, but readily in chloroform, benzene, or light petroleum:

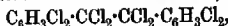
(P) 0.5923 gave 0.9367  $CO_2$  and 0.1212  $H_2O$ .  $C = 43.13$ ;  $H = 2.27$ .

0.327 " 0.7216  $AgCl$ .  $Cl = 54.58$ .

$C_{14}H_8Cl_4$  requires  $C = 43.19$ ;  $H = 2.06$ ;  $Cl = 54.75$  per cent.

\* The study of 4:4'-dichlorotolane tetrachloride was begun by Mr. S. Parrish, B.Sc., at the Royal College of Science. He examined its reduction products, obtaining the *cis*- and *trans*-4:4'-dichlorotolane dichlorides, and prepared from it 4:4'-dichlorobenzil and the corresponding hydrazone. Unfortunately, he was unable to complete the work, and the investigation has been taken up afresh by the present authors. Analyses prefixed by the letter P were made by Mr. Parrish.—W. P. W.

## 3: 4: 3': 4'-Tetrachlorotolane tetrachloride,



is formed when 3: 4-dichlorotoluene is chlorinated to the stage of 3: 4-dichlorobenzylidene chloride under conditions such that sulphuric acid used as drying agent could not be carried forward mechanically (Armstrong and Wynne, *private communication*). The tetrachloride in this case did not separate on cooling, but was isolated by extraction with chloroform from the semi-solid residue left after fractionation of the 3: 4-dichlorobenzylidene chloride (b. p. 274–275°). It crystallises from chloroform in small, diamond-shaped plates, which melt at 197°:

0.1214 gave 0.3037 AgCl. Cl = 61.88.

$\text{C}_{11}\text{H}_6\text{Cl}_8$  requires Cl = 61.97 per cent.

4: 4'-Dichlorotolane Tetrachloride from *p*-Chlorobenzotrichloride.

To prepare the tetrachloride, *p*-chlorobenzotrichloride (40 grams), benzene (60 grams), and copper powder (30 grams) were boiled in a reflux apparatus for about six hours until the reaction seemed to be complete. The hot solution, freed from copper powder by filtration, deposited crystals of the tetrachloride and of *p*-chlorobenzoic acid, the latter of which was removed by extraction with sodium carbonate solution. The yield of tetrachloride from 207 grams of the trichloride amounted to 110 grams.

On crystallisation from chloroform, it was obtained in plates identical in appearance, melting point (190°), and composition (Cl = 54.58 per cent.) with the product formed during the chlorination of boiling *p*-chlorotoluene.

When heated at 230°, the tetrachloride decomposes with the elimination of hydrogen chloride, and at a higher temperature, about 270°, chlorine also can be detected in the escaping gas. This decomposition was studied more closely by distilling 5 grams of the tetrachloride under a pressure of 90–130 mm. The first portion of the distillate was a colourless liquid, which passed over at 234°, but the remainder was solid, and, when crystallised from acetone, formed small, rhombic crystals, which melted at 166–167°. This crystalline compound was subsequently identified as cis-4: 4'-dichlorotolane dichloride (p. 1965):

0.192 gave 0.3712  $\text{CO}_2$  and 0.045  $\text{H}_2\text{O}$ . C = 52.72; H = 2.60.

$\text{C}_{14}\text{H}_8\text{Cl}_4$  requires C = 52.85; H = 2.54 per cent.

*Reduction of 4: 4'-Dichlorotolane Tetrachloride.*

The reduction was carried out by suspending the tetrachloride (5 grams) in boiling absolute alcohol (500 c.c.), and adding

gradually during two days zinc dust (4 grams) and glacial acetic acid (30 c.c.). The solution, freed from zinc dust by filtration, deposited, on cooling, very thin, nacreous flakes, amounting in all to 1.5 grams. On analysis, this proved to be 4:4'-dichlorotoluene.

Concentration of the alcoholic filtrate to 150 c.c. furnished material amounting in all to 1.2 grams, which consisted of long, slender, brittle, prismatic needles, and was identified as *trans*-4:4'-dichlorotoluene dichloride. Further concentration gave only small, ill-defined separations, mixed with zinc acetate.

By carrying out the reduction at 50°, instead of at the boiling point, a third substance, crystallising in lustrous, thin, diamond-shaped plates, was obtained in addition to the other two. It was identified as *cis*-4:4'-dichlorotoluene dichloride, but no estimate could be formed of the relative proportion of the two isomerides in the reduction product.

*cis*-4:4'-Dichlorotoluene dichloride,  $C_6H_4Cl \cdot CCl \cdot CCl \cdot C_6H_4Cl$ , is less soluble in alcohol than the *trans*-isomeride. It melts at 166—167°:

(P) 0.1710 gave 0.3087 AgCl. Cl=44.66.

$C_{14}H_8Cl_4$  requires Cl=44.62 per cent.

When reduced in boiling alcoholic solution with zinc dust and acetic acid, it yields 4:4'-dichlorotoluene.

*trans*-4:4'-Dichlorotoluene dichloride dissolves readily in alcohol, and separates from solution in characteristic, prismatic needles. It melts at 86—87°:

(P) 0.354 gave 0.6808  $CO_2$  and 0.0861  $H_2O$ . C=52.45; H=2.70.

0.3347 „ 0.5986 AgCl. Cl=44.25.

$C_{14}H_8Cl_4$  requires C=52.83; H=2.52; Cl=44.65 per cent.

4:4'-Dichlorotoluene,  $C_6H_4Cl \cdot C \cdot C \cdot C_6H_4Cl$ , is much less soluble in alcohol than the two dichlorides, and appears to be dimorphous, as it crystallises from solution sometimes in nacreous flakes, and sometimes in slender needles. Usually it melts at 175—176°, but on one occasion the melting point first observed was 153—154°, which, after solidification of the specimen and re-fusion, rose to and remained constant at 175—176°. On analysis of two different preparations:

(i) 0.1626 gave 0.4064  $CO_2$  and 0.0518  $H_2O$ . C=68.16; H=3.54.

(ii) 0.1710 „ 0.4262  $CO_2$  „ 0.0458  $H_2O$ . C=67.97; H=2.97.

(i) 0.3517 „ 0.4080 AgCl. Cl=28.70.

$C_{14}H_8Cl_2$  requires C=68.02; H=3.26; Cl=28.72 per cent.

$C_{14}H_{10}Cl_2$  „ C=67.47; H=4.05; Cl=28.48 „

These analyses point to the toluene formula, but the production of a toluene, rather than a stilbene or dibenzyl derivative, by reduction of the dichlorotoluene tetrachloride seemed sufficiently remark-

able to require confirmation. Accordingly, chlorine was passed through a solution of the compound in chloroform until no more of the gas was taken up, and, after removal of the solvent, it was found that the product consisted of 4:4'-dichlorotolane tetrachloride in practically quantitative amount. Hence the conclusion is drawn that the reduction product is, as stated, 4:4'-dichlorotolane.

The formation of a tetrachloride during the preparation of *o*-chlorobenzotrichloride from *o*-chlorotoluene was not observed, and as attempts to make 2:2'-dichlorobenzil, which would have furnished a means of obtaining it, were unsuccessful, recourse was had to Fox's process in the hope that it might be isolated from the product of the action of copper powder on *o*-chlorobenzotrichloride.

*Treatment of o-Chlorobenzotrichloride with Copper Powder.*

*o*-Chlorobenzotrichloride (20 grams) was dissolved in benzene (30 grams), and heated with copper powder (15 grams) for twenty-five hours in a reflux apparatus. After filtration, repeated extraction of the residue with benzene, and removal of the benzene by distillation, the residue was allowed to dry on a porous plate for a fortnight.

In spite of many attempts with different solvents, it was not found possible to extract from this residue any substance other than *o*-chlorobenzoic acid (m. p. 136°). As a similar residue from benzotrichloride, when heated at 200° with 80 per cent. acetic acid, gave a relatively large yield of benzil, a portion of this viscid substance was also heated with acetic acid, but furnished only *o*-chlorobenzoic acid. Yet when the part which had not gone into solution in the acetic acid was dried and distilled, it gave both *cis*- and *trans*-2:2'-dichlorotolane dichlorides. It is difficult to resist the conclusion that the tetrachloride is not formed in the condensation, or, if formed, suffers decomposition into the dichlorides under the conditions of the experiment, being less stable than the 4:4'-dichlorotolane tetrachloride, which requires to be heated at above 200° before decomposition into the dichloride takes place.

To confirm Fox's results (*loc. cit.*), a portion of the viscid product was distilled under 11 mm. pressure. Below 210° the distillate was colourless, and solidified on cooling. By crystallisation from light petroleum, it was separated into two portions, the one consisting of clusters of radiate needles, melting at 136°, identical with *o*-chlorobenzoic acid, and the other of prismatic crystals, melting at 172–173°, which proved to be *cis*-2:2'-dichlorotolane

dichloride (Cl=44.73 per cent.). The later distillate was brown, and, after purification, consisted for the most part of the *cis*-dichloride, whilst the residue in the flask, when extracted by light petroleum, yielded large, transparent rhombs, melting at 127–128°, which agreed in properties with the description given of *trans*-2:2'-dichlorotolane dichloride (Cl=44.5 per cent.).

When the *cis*-2:2'-dichlorotolane dichloride is reduced in boiling alcoholic solution with zinc dust and acetic acid under the conditions already described for the 4:4'-isomeride, it is converted into 2:2'-dichlorotolane (m. p. 87°). The same substance is also formed when the dichloride is heated with copper powder at 260°.

4:4'-Dichlorobenzil.—When 4:4'-dichlorotolane tetrachloride is heated with glacial acetic acid (40 c.c.) and water (10 c.c.) at 170° for six hours, it is converted into 4:4'-dichlorobenzil, which separates in the tube in long, slender, yellow needles, and when recrystallised from alcohol was found to melt at 193°. Montagne (*Rec. trav. chim.*, 1902, [ii], 21, 19) gives the melting point as 200°:

(P) 0.3735 gave 0.8162 CO<sub>2</sub> and 0.1039 H<sub>2</sub>O. C=59.60; H=3.09.

(P) 0.2318 „ 0.2305 AgCl. Cl=25.59.

C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>Cl<sub>2</sub> requires C=60.22; H=2.89; Cl=25.42 per cent.

Hantzsch and Glover obtained this compound from the corresponding benzoin, which was formed from *p*-chlorobenzaldehyde by the benzoin condensation (*Ber.*, 1907, 40, 1519). The quantities of materials used and the exact conditions are not given by them, and it may be of interest to note that while studying the benzoin condensation some years ago, Miss E. S. Hooper, B.Sc., failed to isolate the benzoin from this source, although the product, when oxidised by nitric acid, gave a 40 per cent. yield of 4:4'-dichlorobenzil (m. p. 191°), which was identical with that obtained from 4:4'-dichlorotolane tetrachloride (*private communication*).

The *monohydrazone*, C<sub>6</sub>H<sub>4</sub>Cl·C(N·NH·C<sub>6</sub>H<sub>3</sub>)·CO·C<sub>6</sub>H<sub>4</sub>Cl, crystallises from alcohol in small, yellow prisms, and melts at 178°:

(P) 0.0965 gave 6.4 c.c. N<sub>2</sub> (moist) at 20.5° and 758 mm. N=7.52.

C<sub>20</sub>H<sub>14</sub>ON<sub>2</sub>Cl<sub>2</sub> requires N=7.59 per cent.

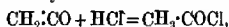
The authors wish to express their thanks to Professor Wynne, who directed their attention to this problem, and has given them much valuable assistance and advice during its investigation.

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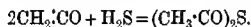
CCIX.—*Some Reactions of Keten. Combination with Hydrocyanic Acid.*

By STELLA DEAKIN and NORMAN THOMAS MORTIMER WILSMORE.

In a note published by Miss F. Chick and one of us (*Proc.*, 1908, **24**, 77), it was stated, among other things, that keten combined with liquid hydrogen chloride under pressure at the ordinary temperature to form acetyl chloride:



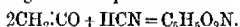
there being no evidence of the formation of the isomeric chloro-acetaldehyde or of its condensation product, dichloroethyl acetate. Under similar conditions keten also combined with hydrogen sulphide, forming acetyl sulphide, the so-called thioacetic anhydride: \*



Finally, it was mentioned that keten reacted with hydrocyanic acid, but that the product was not, as might have been anticipated, acetyl cyanide or pyruvonitrile.

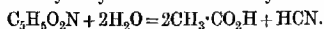
The reaction between keten and hydrocyanic acid has now been further investigated, and a new compound, liquid at the ordinary temperature, has been isolated in a pure state. The actual constitution of this compound has, however, not yet been elucidated; but, as our collaboration has come to an end, and as the substance in question has somewhat remarkable properties, we venture to place on record the results so far obtained.

Analysis and molecular weight, the latter having been found both by the vapour density and the cryoscopic methods, showed the substance to have the empirical formula  $\text{C}_5\text{H}_5\text{O}_2\text{N}$ , its formation taking place according to the equation:



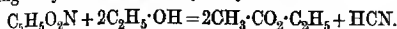
The difficulty in the way of determining its constitution lies in its instability in presence of reagents. For, although it has a boiling point of  $173^\circ$ , and its vapour does not dissociate at the temperature of boiling aniline, it behaves in all the reactions hitherto studied as if it were merely a mixture of keten and hydrocyanic acid, were it not that the velocity of reaction is slower.

Thus with water, either alone or in the presence of acids or alkalis, acetic and hydrocyanic acids are slowly formed:

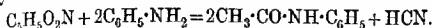


\* In the note referred to there is a misprint, the b.p. of the acetyl sulphide obtained being given as  $55-56^\circ$  instead of  $155-158^\circ$ .

Alcohol in presence of a trace of mineral acid acts in a similar way, giving ethyl acetate and hydrocyanic acid:

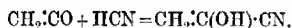


With aniline a violent reaction takes place, acetanilide and hydrocyanic acid being produced:

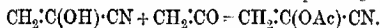


Saturation of an ethereal solution of the substance with hydrogen chloride at a low temperature, followed by cautious addition of water, gave only ammonium chloride together with acetic and formic acids, and an attempt to reduce it by means of hydrogen in presence of platinum black led to no definite result. Obviously therefore the substance is not a derivative of *cyclobutan-1:3-dione*.

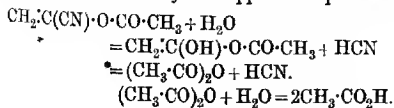
Although we have no very definite experimental evidence to offer in support of it, still we may perhaps be allowed to hazard a guess as to the constitution and mode of formation of the new compound. We may suppose that hydrocyanic acid combines in the first place with a portion of the keten in a way similar to its reaction with aldehydes and ketones to form a cyanohydrin, which in this case would be the nitrile of the unstable  $\alpha$ -hydroxyacrylic acid:



As this nitrile contains a hydroxyl group, the latter would at once react with more keten to form the corresponding acetate:

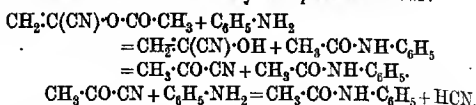


It may be objected to this hypothesis that  $\alpha$ -hydroxyacrylonitrile would change, at least in part, into the well-known isomeric acetyl cyanide or pyruvonnitrile, which should accordingly be found among the products of the reaction. It may well be, however, that at the temperature of the experiment this intramolecular change is comparatively slow, whereas the reaction between keten and hydroxyl is practically instantaneous. A second necessary condition is that the combination of hydrocyanic acid with keten shall be slow, otherwise, with excess of hydrocyanic acid present, there would be no keten available for the second stage of the process. That this condition was fulfilled in our experiments was shown by the fact that a large part of the keten had time to polymerise to *cyclobutan-1:3-dione*, although hydrocyanic acid was present in considerable excess. Following out the hypothesis, the decomposition with water may be supposed to proceed thus:



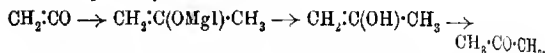


The reaction with aniline may take place as follows:



The reaction with alcohol is less easy to follow, especially as it requires the presence of mineral acid. It may be mentioned that the structure suggested is consistent with the molecular volume, refractivity, and dispersion of the substance.

The actions of Grignard's reagent and of nitrosyl chloride on keten have also been studied. In both cases the keten condensed for the most part to brown, resinous substances, but from the reaction with Grignard's reagent a small quantity of acetone was obtained, probably formed thus:



It was thought that nitrosyl chloride might give nitrosoacetyl chloride or the isomeric oximinoacetyl chloride, but the only substance that could be isolated in a pure state was chloroacetyl chloride.

#### EXPERIMENTAL

##### *Preparation of Ketene and of the Hydrocyanic Acid Derivative.*

The pyrogenic method of preparing ketene, previously described by one of us (Trans., 1907, 91, 1938), has been somewhat improved. Spiral condensers provided with a cylindrical hulk at the lower end are now used in place of the simpler pattern previously illustrated, and it has been found advisable to insert a second trap between the generator and the main condenser. Any ketene which condenses in the traps can be readily distilled over into the main condenser at the end of the operation. The main condenser is kept at  $-110^\circ$  to  $-120^\circ$  by means of a bath of alcohol and ether cooled by suitable addition of liquid air, which is not poured into the bath itself, but into a kind of flattened, metallic test-tube suspended from the top of the Dewar vessel. At a lower temperature the spiral of the condenser becomes rapidly blocked with crystals, while at a higher temperature the condensation of the ketene is incomplete, owing to its dilution with other gases. A platinum wire of about 0.2 mm. diameter and 5 cm. free length has been found to give the best results. With a longer or thicker wire some ketene will be carried away by the increased rush of gas, as the wire must be kept nearly at its melting point in any case. A current of about 7 amperes is used to commence with, but this must be gradually raised to 12 or 14 amperes as the reaction proceeds,

as the wire becomes coated with a layer of conducting carbon. The acetic anhydride is added in charges of about 50 grams, a clean wire being used for each fresh charge. By carefully removing the layer of carbon by crushing it with pliers, one wire may sometimes be made to serve for three charges before breaking. After heating for about an hour and a-half, about half of the acetic anhydride will have disappeared, and the remainder will have become dark brown. The reaction is then stopped, the spent charge is removed, a clean wire is inserted, and a fresh charge of acetic anhydride is poured in. Including subsidiary operations, three or four such charges can be run through in a day, yielding altogether 15 to 20 c.c. of crude keten. The acetic anhydride should be as pure as possible, or the yield will be much reduced; but inferior samples may be greatly improved in this respect by previously distilling from phosphoric oxide. Keten may also be prepared from acetone, but is then very impure. Strange to say, glacial acetic acid appears to be quite unacted on by the hot wire.

To prepare the hydrocyanic acid derivative, 15 to 20 c.c. of keten were distilled into an exhausted bomb tube cooled in liquid air. About twice this quantity of anhydrous hydrocyanic acid was added, and the tube was then sealed off before the blowpipe. The hydrocyanic acid was prepared by the action of 50 per cent. sulphuric acid on potassium cyanide, and was dried by passing it through a long column of calcium chloride. It was stored in a bulb provided with two taps, from which it could be distilled into the bomb tubes as required. As there was an interval of only about  $10^{\circ}$  between the melting point of the hydrocyanic acid and the temperature at which the keten began rapidly to polymerise, arrangements had to be made to keep the keten cold until the hydrocyanic acid had melted, and then to mix the two liquids as rapidly as possible. Accordingly, on removing the bomb tube from the liquid air, the lower end containing the keten was well jacketed in wool, the upper part containing the hydrocyanic acid being left exposed to the air, and the tube was placed in an inclined position in a shaking machine and shaken for about two hours, or until it had attained the temperature of the room. It was then placed in an ice-safe until wanted. Since considerable pressure was necessarily developed in the tubes as the temperature rose, to minimise the effects of a possible explosion, the shaking and removal to the ice-safe were attended to by one of us at times when the laboratory was otherwise unoccupied. The contents of the tubes were only slightly coloured brown, showing that much less brown resin had been formed than when keten polymerises in the ordinary way. Before opening, the tubes were again cooled to  $-78^{\circ}$ , when, as the contents had

solidified, they could be opened with impunity, and they were then removed from the bath and allowed to attain the temperature of the room. As the contents showed the marked tendency to bump characteristic of hydrocyanic acid, a capillary tube connected with a source of dry hydrogen was passed down to the bottom of the bomb-tube as soon as the contents were sufficiently melted. With the help of the current of hydrogen, most of the hydrocyanic acid was then distilled off, the tube being finally warmed to about 50° in a water-bath. The contents of three such tubes were fractionally distilled under 100 mm. pressure, a Claisen flask being employed, to the second neck of which a Young's "pear" still-head with four bulbs had been sealed. The liquid separated mainly into two fractions, one boiling at about 70–80°, which was chiefly cyclobutan-1:3-dione, and the other boiling at 100–110°, which contained the bulk of the new substance. Some brown residue was left in the flask, and crystals of dehydracetic acid, which were identified in the usual way, and which were due to the polymerisation of cyclobutan-1:3-dione, were deposited in the neck of the flask and lower portion of the still-head. After repeated fractionation of the portion of higher boiling point, 7 grams of a colourless liquid were obtained, which boiled constantly at 110·0–110·4°/100 mm. (corr.), this being the yield from about 50 c.c. of crude keten. The fractionation was carried out in dry hydrogen. Carbon dioxide was unsuitable for this purpose, as it was very soluble in the liquid.

*Composition and Properties of the Hydrocyanic Acid Derivative.*

The carbon and hydrogen were determined by the method previously used for "acetylketen" (Trans., 1908, 63, 947). Attempts to estimate the nitrogen by the Kjeldahl method were unsuccessful owing to loss of hydrocyanic acid, and a modification of the Dumas method was therefore employed. The substance was weighed in an exhausted thin-walled glass bulb, the weight of the air removed from the bulb (0·66 c.c. = 0·8 milligram) being added to the apparent weight of the substance. The bulb was packed in copper oxide in the combustion tube, and, when all the air in the latter had been swept out with carbon dioxide, it was broken by means of a pointed glass rod attached to the inlet tube. The vapour density was determined by the Hofmann method, using freshly distilled aniline in the outer jacket. The volume observed was corrected for the gas and vapour driven off from the walls of the endiometer, and, in measuring the pressure, allowance was made for the temperature of the mercury column and for the vapour pressure of mercury at 184°, the boiling point of aniline under 756·7 mm. pressure. The volume remained constant for about

half an hour, showing that the vapour of the substance was stable at the temperature of boiling aniline. The benzene used in determining the molecular weight by the cryoscopic method had been previously distilled from sodium:

0.1705 gave 0.3393  $\text{CO}_2$  and 0.0672  $\text{H}_2\text{O}$ .  $\text{C}=54.2$ ;  $\text{H}=4.4$ .  
 0.1369 " 0.2702  $\text{CO}_2$  " 0.0580  $\text{H}_2\text{O}$ .  $\text{C}=53.8$ ;  $\text{H}=4.7$ .  
 0.1999 " 21.7 c.c.  $\text{N}_2$  (dry) at  $14.8^\circ$  and 755.1 mm.  $\text{N}=12.8$ .  
 0.0859 " 58.6 c.c. at  $184^\circ$  and 375.9 mm.  $\text{M.W.}=111.2$ .  
 0.0882, in 16.93 benzene, gave  $\Delta t = -0.260^\circ$ .  $\text{M.W.}=100.2$ .  
 0.0697, " 16.93 " "  $\Delta t = -0.186^\circ$ .  $\text{M.W.}=110.8$ .  
 0.1157, " 16.93 " "  $\Delta t = -0.298^\circ$ .  $\text{M.W.}=114.8$ .  
 $\text{C}_5\text{H}_5\text{O}_2\text{N}$  requires  $\text{C}=54.1$ ;  $\text{H}=4.5$ ;  $\text{N}=12.6$  per cent.  
 $\text{M.W.}=111.04$ .

Under 772 mm. pressure, the liquid boiled at  $173^\circ$  (corr.), but it began to turn brown a little below that temperature. On cooling, a white opalescence appeared at about  $-45^\circ$ , which disappeared again on warming to  $-42^\circ$ , but this must have been due to a trace of moisture or other impurity, as the substance remained liquid, although it became very viscous, down to  $-78^\circ$ . On cooling with liquid air, it froze to a white solid, which melted at  $-196^\circ$  to  $-195^\circ$ . Owing to the presence of the opalescence, the melting point could not be found by visual observation, but it was readily determined by means of a thin wire, moisture being excluded by jacketing the wire with calcium chloride in the upper part of the tube. On repeated trials, the wire was found to be immovable up to  $-196^\circ$ , but it could be moved up and down at  $-195^\circ$ .

The density was determined at various temperatures. Two samples of the substance were used, the first of which had been distilled some weeks, and the second a few days before the experiment. The densities in each series lie very nearly on a straight line, but there is a difference of about five parts in 10,000 between the two series. As a mean of four weighings, the pycnometer contained 0.74325 gram of water weighed in air at  $18^\circ$ . The temperatures in the table have been corrected to the hydrogen scale:

$t$ .	Weight of substance in air.		$d_4^t$ .	
	I.	II.	I.	II.
9.3°		0.7597		1.0746
10.0	0.7995		1.0743	
13.0		0.7960		1.0695
14.2	0.7961		1.0697	
16.6		0.7937		1.0664
18.5	0.7925		1.0647	
21.3		0.7901		1.0614
22.9	0.7889		1.0598	
24.8		0.7870		1.0571
29.9	0.7833		1.0521	
30.3		0.7823		1.0511

Taking the mean of the two series by graphic interpolation, the density of the liquid between 10° and 30° is given by the equation:

$$d_4 = 1.0685 - 0.00112 (t - 15^\circ).$$

Consequently, assuming the molecular weight to be 111.04, the molecular volume at 15° is 103.9, whereas the molecular volume calculated for the formula  $\text{CH}_2\text{C}(\text{CN})\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$  from Traube's values for the atomic volumes (Traube, *Grundriss der physikalischen Chemie*, 1904, p. 120; Smiles, *Chemical Constitution and Physical Properties*, 1910, p. 125) is 100.2.

The refractive indices of the same two samples were measured by means of the Pulfrich refractometer. The densities were obtained by interpolation from the values given above, the two series being kept separate:

Line.	Sample.	$t$ .	$d_4$ .	$N_D$ .	M.R.
C.	I.	16.9°	1.0667	1.42443	23.580
C.	II.	22.6	1.0598	1.42150	25.598
D.	I.	16.0	1.0676	1.42771	23.784
D.	II.	23.1	1.0592	1.42435	25.771
G.	II.	22.5	1.0599	1.43756	27.478

Taking the mean of the two series, and using the values for the atomic refractivities and dispersions given in Landolt and Börnstein's "*Tabellen*," we obtain the following values for the molecular refractivity and dispersion:

	$C$	$D$	$G - C$
Found ... ..	26.59	26.75	0.16
Calculated for $\text{CH}_2\text{C}(\text{CN})\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$	26.34	26.49	0.15

At the ordinary temperature the hydrocyanic derivative is a colourless, somewhat oily liquid. It has a rather pleasant, although slightly pungent odour, resembling that of the nitriles. It is readily miscible with all the ordinary organic solvents, but is sparingly soluble in cold water. It is more readily soluble in hot water, separating again as an emulsion on cooling. It is, however, slowly decomposed and dissolved by water on keeping, even in the cold, acetic and hydrocyanic acids being formed, and this whether the aqueous solution was originally neutral, acid or alkaline; but on warming it with aqueous alkalis or sodium carbonate, some brown substance is also formed. This hydrolysis has been studied quantitatively in both acid and neutral solution. Since methyl-orange cannot be used as an indicator for acetic acid, and phenolphthalein is useless in presence of soluble cyanides, the following method of titration was adopted. Standard alkali free from carbonate was first added in slight excess, that is, in the proportion of rather more than three equivalents of alkali to one molecule of the substance, and the cyanide was titrated with standard silver

nitrate, the end-point being shown, as usual, by the formation of a permanent opalescence. A second equal volume of silver solution was then added, in order to replace all the  $\text{CN}'$  in solution by  $\text{NO}_3'$ , after which the excess of alkali could be found by means of standard acid and phenolphthalein. Proceeding in this way, the alkali used corresponded with the hydrocyanic as well as with the acetic acid, so that, to find the amount of the latter, the hydrocyanic acid as found from the silver titration had to be subtracted from the total acid. To carry out the hydrolysis in acid solution, a weighed amount of the substance was placed in a stoppered flask, together with 50 c.c. of water and 1 c.c. of 0.1092*N*-sulphuric acid. The mixture was kept overnight, warmed for a few minutes on the water-bath, cooled, and titrated, the sulphuric acid being allowed for. The silver nitrate was 0.1*N*, and the alkali 0.1055*N*:

0.3041 required 13.33 c.c. silver and 76.91 c.c. alkali; or 1 mol. gave 0.973 mol. HCN and 1.988 mol.  $\text{C}_2\text{H}_4\text{O}_2$ .

0.2943 required 12.90 c.c. silver and 72.69 c.c. alkali; or 1 mol. gave 0.973 mol. HCN and 1.919 mol.  $\text{C}_2\text{H}_4\text{O}_2$ .

For the hydrolysis in alkaline solution, the substance was added at once to excess of the standard alkali. After about two hours at the ordinary temperature, the reaction appeared to be complete, and the solution was titrated:

\* 0.2820 required 12.16 c.c. silver and 70.85 c.c. alkali; or 1 mol. gave 0.967 mol. HCN and 1.975 mol.  $\text{C}_2\text{H}_4\text{O}_2$ .

0.3142 required 13.86 c.c. silver and 80.80 c.c. alkali; or 1 mol. gave 0.979 mol. HCN and 2.032 mol.  $\text{C}_2\text{H}_4\text{O}_2$ .

The reaction is thus not quite quantitative, but it is sufficiently so to prove the validity of the equation given on p. 1968.

An attempt was next made to hydrolyse the CN group without breaking up the molecule. 2.33 Grams of the compound were dissolved in about 20 c.c. of dry ether; the solution was cooled to  $-78^\circ$ , and dry hydrogen chloride was passed in until two layers began to separate, the lower one being a solution of ether in liquid hydrogen chloride. Two molecular proportions of water, dissolved in 20 c.c. of ether and cooled to  $-78^\circ$ , were then added, and the mixture was kept overnight, the temperature gradually rising to about  $0^\circ$ . As no reaction appeared to have taken place, even on warming to the boiling point of ether, a third molecular proportion of water was added, and ether was evaporated until water began to separate. On again keeping overnight at the ordinary temperature, ammonium chloride crystallised out, and the solution was then fractionally distilled. After the ether had been expelled, a fraction passed over at  $85-103^\circ$ , which gave all the reactions of formic acid. A second fraction, which passed over at  $103-135^\circ$ ,

was also acid. It was redistilled from concentrated sulphuric acid to destroy any formic acid, and it then answered to the tests for acetic acid. A small quantity of liquid which still remained in the flask was heated under a pressure of 35 mm. to  $230^{\circ}$ , but it merely charred without distilling. The hydrolysis of the hydrocyanic acid derivative had therefore followed practically the same course as in aqueous solution.

The substance did not appear to react with absolute alcohol, but on adding dry hydrogen chloride the odour of ethyl acetate was noticed. On treating another portion of the alcoholic solution with lime, a vigorous reaction took place, hydrocyanic acid and ethyl acetate being given off. To a larger portion of the solution a small quantity of ethylsulphuric acid was added, and the mixture was left for two days, when hydrocyanic acid and ethyl acetate were again noticeable. On passing a current of dry air through the solution and then into water, hydrocyanic acid was readily identified in the latter. The alcoholic solution was then boiled for some time over phosphoric oxide in a flask fitted with a reflux condenser, and finally distilled, when, after all the hydrocyanic acid had been driven off, a sample of ethyl acetate was obtained, which boiled steadily at  $77^{\circ}$  (corr.).

The compound reacted vigorously with aniline, hydrocyanic acid being given off, and a solid substance being formed, which proved to be acetanilide, melting at  $113^{\circ}$  (corr.). This was confirmed by taking a mixed melting point with a sample of pure acetanilide from other sources. The reaction appeared to be quantitative.

#### *Action of Grignard's Reagent on Keten.*

The reagent (magnesium methyl iodide) in dilute ethereal solution was cooled to  $-50^{\circ}$ , and gaseous keten was slowly passed in. A very vigorous reaction took place, and much heat was evolved, as was shown by the amount of solid carbon dioxide which was required to maintain the low temperature. As only resinous substances appeared to be formed, the experiment was repeated, but this time the keten was largely diluted with dry hydrogen, the dilution being effected by passing the hydrogen through liquid keten at  $-78^{\circ}$  to  $-70^{\circ}$ . The ethereal solution became dark reddish-brown and very viscous, and a yellow, resinous solid separated. The mixture was decomposed with powdered ice, and the magnesium hydroxide was dissolved by addition of dilute hydrochloric acid, leaving a considerable amount of brown resin, which was not soluble in either the water or the ether. This was removed by filtration, and the filtrate was fractionally distilled. After the ether had been removed, a small quantity of liquid passed over at about

100°, which had a strong odour of acetone. The presence of acetone was confirmed by the iodoform reaction, by the alkaline mercuric chloride and nitroprusside tests, and by the formation with benzaldehyde of distyryl ketone (m. p. 111–112°, corr.). No other compound could be isolated.

#### *Action of Nitrosyl Chloride on Keten.*

The nitrosyl chloride was prepared by passing nitric oxide into liquid chlorine at about  $-60^{\circ}$  until saturated. The chlorine was obtained from hydrochloric acid and potassium permanganate. It was washed with water and dried with sulphuric acid. The nitric oxide was produced by the action of nitric acid on copper, and was purified by passing first through 50 per cent. potassium hydroxide solution and then through concentrated sulphuric acid. The nitrosyl chloride was fractionally distilled before use to remove any excess of chlorine.

At first, attempts were made to carry out the reaction by condensing the keten with excess of nitrosyl chloride in bomb-tubes by means of liquid air, and allowing the temperature gradually to rise, but violent explosions took place as soon as the nitrosyl chloride melted. Accordingly, another method was tried, gaseous keten being passed slowly into excess of nitrosyl chloride at a temperature just above the melting point of the latter ( $-61^{\circ}$ ). Vigorous reaction took place at once, with evolution of much heat, hydrogen chloride and an odour of carbonyl chloride being given off, and a white solid separating out, which melted at about  $-50^{\circ}$ . If the temperature was allowed to rise during the reaction, much gas was evolved, which, on analysis, proved to be a mixture of hydrogen chloride, carbonyl chloride, carbon dioxide, acetylene, and nitrogen. The acetylene and some or all of the carbon dioxide were impurities in the original keten. The gas did not contain nitric oxide. After all the keten had been added, the temperature was allowed to rise, and a current of hydrogen was passed through the mixture in order to remove the excess of nitrosyl chloride, when a dark brown, very viscous liquid was left. On distilling this under a pressure of 95 to 100 mm., a colourless liquid passed over at  $58-68^{\circ}$ . This liquid did not contain nitrogen. Under atmospheric pressure it boiled at  $106^{\circ}$ . It reacted with water to form chloroacetic acid, and with aniline it gave chloroacetanilide, melting at  $133^{\circ}$ , which was confirmed by taking a mixed melting point with a sample of chloroacetanilide from another source. The colourless liquid was therefore chloroacetyl chloride, in the formation of which the nitrosyl chloride had apparently acted merely as a source of chlorine. A large quantity of a brown, resinous substance was left in the distilling



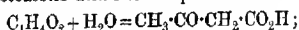
mask. This was found to contain nitrogen, but a definite compound could not be obtained from it. Attempts to obtain a clean reaction by previously diluting the nitrosyl chloride with dry ether met with no better success.

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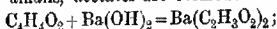
CCX.—*The Polymerisation of Keten. cycloButan-1:3-dione ("Acetylketen").*

By FRANCES CHICK and NORMAN THOMAS MORTIMER WILSMORE.

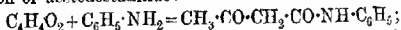
In a previous paper (Trans., 1908, 93, 946) we stated that when keten, either in the liquid or the gaseous state, is left to itself at the ordinary temperature, a brown substance is formed, the chief constituent of which is a colourless liquid of a very pungent odour, boiling at 126—127°/760 mm. (corr.), and which, after having been frozen, melts at  $-7^{\circ}$  to  $-6^{\circ}$ ; and we showed by combustion analyses, by determination of the vapour density according to the Hofmann method, and by measurement of the freezing point of its solution in benzene, that this liquid is a polymeride of keten, formed according to the equation  $2\text{CH}_2\text{:CO} = \text{C}_4\text{H}_4\text{O}_2$ . We also showed that the substance undergoes a series of reactions which indicate a close relation with acetoacetic acid. Thus, with water in the cold, acetoacetic acid itself is produced:



on boiling with alkalis, acetates are formed:



with aniline, a very vigorous reaction takes place, resulting in the formation of acetoacetanilide:



and with phenylhydrazine, a phenylhydrazone-phenylhydrazide of acetoacetic acid is obtained:



The hydrazide character of the latter substance was shown by the formation of a hydrochloride and of a platinichloride. Addition of pyridine to the polymeride caused a violent reaction, with the formation of brown resins; but when the reaction was allowed to take place in benzene solution, dehydracetic acid was the chief product.

All these facts led us to conclude that the polymeride still

contained a keten group, and we therefore assumed it to be acetylketen, having the formula  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}$ . At the same time, we considered the possibility of its being *cyclobutan-1:3-dione*:

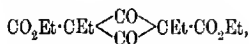


as this would agree better with our observation that it did not appear to react with alcohol. Nevertheless, the great reactivity and very unsaturated nature of the substance led us to prefer the keten formula, and a measurement of the refractive index also seemed to support this choice:

	M.R.
$\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}$ .....	29.489
$\text{CH}_2 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH}_2$ .....	18.782
$\text{CH} \begin{array}{c} \diagup \text{C(OH)} \diagdown \\ \diagdown \text{C(OH)} \diagup \end{array} \text{CH}$ .....	20.664
Found .....	20.675

Here, however, we had to suppose that the  $\cdot\text{CH}\cdot\text{CO}$  group had a depressing action on the refractive index, an assumption which, on account of lack of experimental evidence, we made with all reserve.

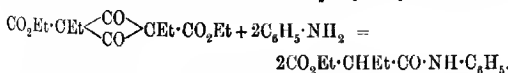
After the publication of the previous paper, the work was for a time interrupted, and it was not until the session just closed that it could be seriously resumed. In the meantime a paper by Staudinger and Bereza has appeared (*Ber.*, 1909, **42**, 4908), in which the polymerisation of the disubstituted keten, ethyl ethylketencarboxylate,  $\text{CO}\cdot\text{CEt}\cdot\text{CO}_2\text{Et}$ , is described, the product according to these authors being undoubtedly a *cyclobutane* derivative, namely, ethyl 1:3-diethyl*cyclobutan-2:4-dione-1:3-dicarboxylate*,



and on this and other grounds they conclude that the substance discovered by us must be  $\Delta^1$ -*cyclobuten-1-ol-3-one*,

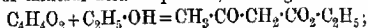


The arguments of Staudinger and Bereza did not, however, seem to us to be necessarily convincing. Thus, ethyl 1:3-diethyl*cyclobutan-2:4-dione-1:3-dicarboxylate* reacts with two molecular proportions of aniline to form two molecules of ethyl ethylmalonanilate:



Also, on heating, the diethyl ester dissociates with regeneration

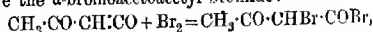
of ethyl ethylketencarboxylate. Our substance, on the other hand, reacts with only one molecular proportion of aniline, and it shows no tendency to dissociate on heating—quite the contrary. Similar remarks apply also to the reactions of truxilic acid referred to by Staudinger and Bereza in this connexion. Again, the comparative stability of the polymeride of keten, both in the pure state and in alcoholic solution, which Staudinger and Bereza cite as being inconsistent with the keten formula, was not conclusive, more especially as our previous observations on these points were incomplete. We have since found that alcohol reacts with the polymeride if a trace of mineral acid be present, forming acetoacetic ester:



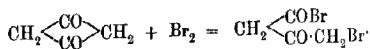
and that, when the pure substance is kept for some weeks in sealed tubes at the ordinary temperature, dehydracetic acid is formed, apparently by direct polymerisation. Moreover, Staudinger and Bereza show that disubstituted ketens become much less reactive when one of the substituents is an acidic group, and, consequently, it was not unreasonable to assume, as we did, that the substitution of acetyl for a hydrogen atom in keten should have a similar effect.

So far therefore there was not sufficient evidence available to allow of a definite conclusion being drawn between the open chain and the cyclic formula for the first polymeride of keten. Most of the reactions described above involved a transference of a hydrogen atom from the reagent to the polymeride, and there was nothing to show into which part of the molecule of the latter this atom had entered.

It occurred to us that a study of the action of bromine on the polymeride might throw some light on its constitution. We found that bromine combined directly with the substance, forming a monobromoacetoacetyl bromide, which, on treatment with alcohol, gave the corresponding ethyl monobromoacetoacetate. If the polymeride had the acetylketen structure, addition of bromine should give the  $\alpha$ -bromoacetoacetyl bromide:



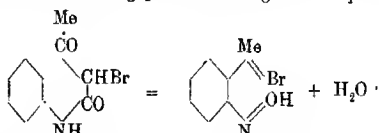
whereas from *cyclobutan-1:3*-dione only the  $\gamma$ -derivative could result:



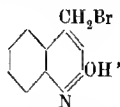
Since we have actually obtained the  $\gamma$ - and not the  $\alpha$ -derivative under conditions which rendered a wandering of the bromine atom from the  $\alpha$ - to the  $\gamma$ -position highly improbable, it follows that the evidence in favour of the cyclic structure for the first polymeride of keten is now conclusive. It may be noted, however, in passing, that the substance may still be regarded as an internal anhydride

of acetoacetic acid. The true acetylketen has therefore yet to be discovered, but we venture to prophesy that, when prepared, it will resemble *cyclobutan-1:3-dione* in many of its reactions.

Incidentally, by treating the above-mentioned  $\gamma$ -bromoacetoacetyl bromide with aniline, we have obtained the same bromoacetoacetanilide as was prepared by Knorr (*Annalen*, 1886, **236**, 79) by the bromination of acetoacetanilide, and, by digesting this with concentrated sulphuric acid as described by him, we also obtained his bromo-2-hydroxy-4-methylquinoline (*loc. cit.*, p. 91). Knorr also prepared a substance, which he believed to be identical with the latter compound, by the action of bromine water on 2-hydroxy-4-methylquinoline itself. As under these conditions the bromine would almost certainly occupy the 3-position, Knorr assumed that his bromoacetoacetanilide was the  $\alpha$ -derivative, the condensation with sulphuric acid taking place according to the equation:

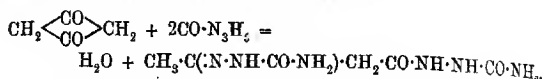


We now find, however, that the compound formed on brominating 2-hydroxy-4-methylquinoline is not identical with, but is an isomeride of, the bromo-2-hydroxy-4-methylquinoline produced by the action of sulphuric acid on bromoacetoacetanilide; and, since our synthesis shows that the latter substance undoubtedly has the bromine in the  $\gamma$ -position, it follows that the compound obtained from it by the action of sulphuric acid is  $\alpha$ -bromo-2-hydroxy-4-methylquinoline:

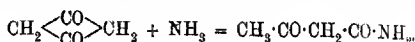


The semi-enolic formula,  $\text{CO} \langle \text{CH}_2 \rangle \text{C} \cdot \text{OH}$ , proposed by Staudinger and Bereza agrees better than the diketonic formula,  $\text{CO} \langle \text{CH}_2 \rangle \text{CO}$ , with the molecular volume, refractive index, and dispersion of the substance, as we shall show later; but we can find no chemical evidence for it. *cyclobutan-1:3-dione* does not appear to react with sodium, with acetyl chloride, or with phenylcarbimide. In fact, a mixture of it with phenylcarbimide may be separated into its constituents by fractional distillation. It may be mentioned, however, in this connexion that the substance gives a red colour with ferric chloride in alcoholic solution. The semi-enolic formula

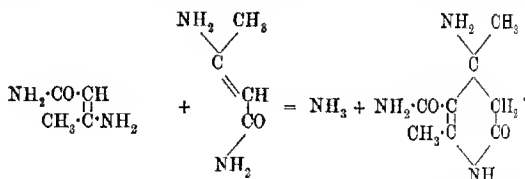
is also inconsistent with the reaction with phenylhydrazine, this substance reacting normally with  $\beta$ -diketones, which can exist in the semi-enolic form to form a pyrazole ring. The reaction with phenylhydrazine is supported by that with semicarbazide, two molecular proportions of which react with *cyclobutan-1:3-dione* to form a semicarbazone-semicarbazide of acetoacetic acid:



Dry ammonia combines with *cyclobutan-1:3-dione* at low temperatures to form acetoacetamide, previously prepared by Claisen and Meyer (*Ber.*, 1902, 35, 583) by the prolonged action of dilute aqueous ammonia on acetoacetic ester:



By the further action of dry ammonia, acetoacetamide is converted into a yellow oil. This oil could not be purified, but it appeared to consist mainly of the hitherto non-isolated amide of  $\beta$ -amino-crotonic acid,  $\text{CH}_3\cdot\text{C}(\text{NH}_2)\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}_2$ , for, on heating it in a current of dry hydrogen, a crystalline substance was produced, melting at  $197^\circ$ , and having the empirical formula  $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_2$ . From analogy to the condensation of acetoacetamide described by Claisen and Meyer, this crystalline substance is probably 4-amino-2:4-dimethyl- $\Delta^2$ -tetrahydro-6-pyridone-3-carboxylamide, formed thus:



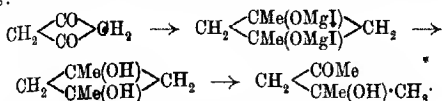
From its reactions the stability of the *cyclobutan-1:3-dione* ring is thus seen to be very small, even when compared with that of *cyclobutane* prepared by Willstätter and Bruce (*Ber.*, 1907, 40, 3979). In fact, the substance behaves as if the ring were not completely closed, that is to say, as if its constitution were:



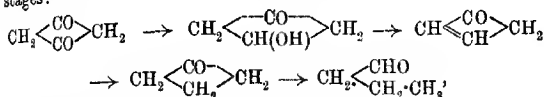
Since, however, there is no precedent for such a formula as this, we are not prepared seriously to propose it.

The action of Grignard's reagent (in this case magnesium methyl iodide) gave for the most part only by-products which could not be

identified, but there was some indication of the formation of diacetone alcohol, which was probably produced somewhat as follows:



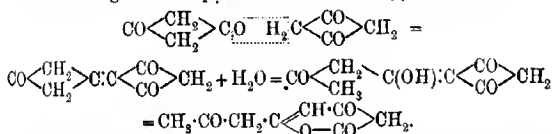
Reduction of *cyclobutan-1:3-dione* with hydrogen in the presence of platinum black gave an unlooked-for result, *n*-butyraldehyde being formed. The reaction may possibly take place in the following stages:



or  $\text{C}_4\text{H}_4\text{O}_3 + 6\text{H} = \text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO} + \text{H}_2\text{O}$ .

As the intermediate compounds have not been isolated, it is not possible to say exactly at what stage the ring is broken. The elimination of water would be facilitated by the dehydrating action of unchanged *cyclobutan-1:3-dione*.

The further polymerisation of *cyclobutan-1:3-dione* to dehydracetic acid may perhaps be represented by the following scheme, although many others are possible, especially if *cyclobutan-1:3-dione* be given the open-chain structure suggested above:

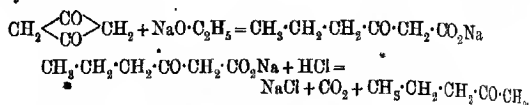


Collie's formula for dehydracetic acid (*Trans.*, 1891, 59, 179) has here been chosen. The condensation would be much more difficult to follow if dehydracetic acid had the formula assigned to it by Feist (*Annalen*, 1890, 257, 253).

Much work has been done with a view to discovering the constitution of the yellow substance which is formed from *cyclobutan-1:3-dione* in the presence of quinoline; but, on account of the small quantity available, not much success has been obtained.

In our former paper we stated that "acetylketen" combined with sodium ethoxide in dry alcohol to form sodium ethylacetoacetate, which, on boiling with hydrochloric acid, gave carbon dioxide and methyl propyl ketone. Since the polymeride of keten is in reality *cyclobutan-1:3-dione*, the compound formed with sodium ethoxide must have been sodium butyrylacetate, which,

however, would also give methyl propyl ketone on boiling with hydrochloric acid:



We propose to study this type of reaction more fully.

*cyclobutan-1:3-dione* does not react with hydrocyanic acid, even when the two substances are heated on the water-bath in sealed tubes, and it does not react with liquid cyanogen at the ordinary temperature.

#### EXPERIMENTAL.

##### *Preparation of cyclobutan-1:3-dione.*

We have not succeeded greatly in improving the yield of *cyclobutan-1:3-dione*, about 5 grams from 150 grams of acetic anhydride being the best hitherto obtainable. It is not necessary to fractionate the crude keten, beyond allowing the temperature to rise to about  $-80^\circ$  to  $-70^\circ$ , before distilling it into the pressure tubes. There seems to be little risk of explosion if the tubes are carefully made, and they may be handled with safety after polymerisation has taken place, as the internal pressure will then have diminished. They should, however, be re-cooled to about  $-80^\circ$  before being opened, or loss of substance may be caused by the rush of gas. Diluting the keten with ether to diminish the violence of the polymerisation did not noticeably improve the yield; but, on the other hand, surrounding the tube containing the keten with a bath of alcohol cooled to  $-30^\circ$ , or lower, and allowing the whole slowly to attain the temperature of the room, materially reduced the formation of brown resins. To ensure complete polymerisation, the tubes should be kept for a day or two before being opened. The distillation of the *cyclobutan-1:3-dione* is conveniently carried out under about 30 mm. pressure, when the bulk of the substance passes over as the temperature of the bath rises from  $40^\circ$  to  $60^\circ$ . The temperature should, however, finally be raised to about  $100^\circ$ . The liquid then remaining in the distilling flask consists of dehydracetic acid and brown resins. The distilling flask should be heated by a water- or oil-bath, and not by a naked flame, or the distillate may be contaminated with decomposition products from the residue. The whole apparatus should, of course, be carefully dried and filled with dried air before commencing the distillation; and only dried air should be allowed to enter the apparatus during and at the close of the operation. These precautions are especially necessary when it is intended to study the physical properties of the sub-

stance. The preparation of *cyclobutan-1:3-dione* may be recommended as a useful exercise for students in laboratories where a supply of liquid air is available.

*Physical Properties of cyclobutan-1:3-dione.*

We have confirmed the boiling point of *cyclobutan-1:3-dione* under 760 mm. pressure previously given. Under 100 mm. pressure the substance boils at 69—71° (corr.). The freezing point of a carefully prepared sample was found to be -7.9° to -7.5°.

The density of two samples of the substance was determined at various temperatures. As a mean of four weighings (0.7432, 0.7433, 0.7432, 0.7433), the pycnometer contained 0.74325 gram of water weighed in air at 18°. The weights of *cyclobutan-1:3-dione* and the densities calculated from these were as follows:

t.	Weight of substance in air.		$d_t$ .	
	I.	II.	I.	II.
9.5°		0.8238		1.1069
10.5	0.8226		1.1053	
14.1		0.8196		1.1012
14.3	0.8193		1.1008	
17.7	0.8165		1.0969	
18.7		0.8157		1.0958
21.6	0.8130		1.0921	
22.7		0.8123		1.0912
25.3	0.8098		1.0877	
26.7		0.8088		1.0864
29.3	0.8064		1.0830	

The temperatures were measured by means of a thermometer which had been carefully compared with a standard thermometer from the International Bureau of Weights and Measures, and they have been corrected to the hydrogen scale. The densities in each series lie very nearly on a straight line, but there is a difference of from 2 to 4 parts in 10,000 between the two series. The density at 23°, given in our previous paper, is in line with those in the first series. Taking the mean of the two series by graphic interpolation, the density of *cyclobutan-1:3-dione* between 10° and 30° is given by the equation:





$$d_t = 1.1000 - 0.00118(t - 15^\circ).$$

Taking the molecular weight as 84.03, the molecular volume at 15° is 76.39. Assuming Traube's values for the atomic volumes at 15° (Traube, *Grundriss der physikalischen Chemie*, 1904, p. 120; Smiles, *Chemical Constitution and Physical Properties*, 1910, p. 125): C=9.9; H=3.1; O<sub>CO</sub>=5.5; O<sub>OH</sub>=2.3; ring formation = -8.1,



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and molecular co-volume=25.9, we obtain the following calculated values:

	M.V. 15.
 .....	80.8
 .....	77.5
 .....	74.4
 .....	88.9
Found.....	76.4

This property is therefore decisively in favour of a cyclic formula. The enolic formulae appear to agree better than the diketonic formula, but it is quite possible that the contraction due to the formation of the *cyclobutano* ring is more than 8.1 units, this number having been obtained mainly from a study of benzenoid substances.

The refractive index of *cyclobutan*-1:3-dione has been re-determined, using portions of the two samples just mentioned, with the result that the value for the *D* line given in our former paper would seem to have been too low. This may have been due to the precautions to exclude moisture having been insufficient. The densities were interpolated from the values given above:

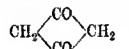
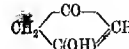
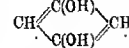
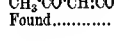
First Sample.

Line.	<i>t.</i>	<i>N.</i>	<i>d<sub>20</sub></i>	M.R.
<i>C</i>	18.7°	1.43490	1.0957	20.007
<i>D<sub>1</sub></i>	19.2	1.43769	1.0951	20.131
<i>G'</i>	18.7	1.45179	1.0957	20.680

Second Sample.

<i>C</i>	18.6°	1.43547	1.0958	20.020
<i>D<sub>1</sub></i>	18.3	1.43877	1.0961	20.157
<i>G'</i>	18.7	1.45236	1.0957	20.702

Both sets of numbers give as the value for the molecular "dispersion," 0.673. For comparison, the values for the molecular refractivities and dispersion, calculated from the atomic refractivities given in Landolt and Börnstein's "*Tabellen*" for the various isomeric formulae, will be found in the table herewith:

	<i>C.</i>	<i>D<sub>1</sub></i>	<i>G' - C.</i>
 .....	18.53	18.78	0.47
 .....	19.54	19.72	0.61
 .....	20.56	20.66	0.80
 .....	20.36	20.49	0.70
Found.....	20.02	20.14	0.67

From these figures it would appear that of the possible ring formulae the semi-enolic modification is the most probable. The very unsaturated nature of the substance, however, makes it legitimate to assume the existence of an exaltation of the refractive index and dispersion which would raise the values calculated for the diketonic formula by an amount rather less than that due to a double bond.

The study of the absorption spectrum has been kindly repeated for us by Professor E. C. C. Baly, using various thicknesses of a 0.1 molar solution in dry ether. The result was to confirm the observation of Mr. H. E. Watson given in our former paper. There was no selective absorption, and only a slight general absorption in the ultra-violet.

*Analysis of cyclobutan-1: 3-dione.*—As a further check on the composition, a third analysis of the substance was made:

0.1298 gave 0.2704  $\text{CO}_2$  and 0.0599  $\text{H}_2\text{O}$ .  $\text{C}=56.8$ ;  $\text{H}=5.1$ .

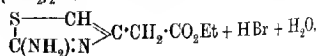
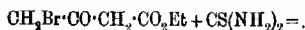
$\text{C}_4\text{H}_4\text{O}_2$  requires  $\text{C}=57.1$ ;  $\text{H}=4.8$  per cent.

*Action of Alcohol on cyclobutan-1: 3-dione.*—As stated earlier in the paper, cyclobutan-1: 3-dione combines with ethyl alcohol in the presence of a trace of mineral acid. To about 0.5 gram of the compound dissolved in ethyl alcohol, a small quantity of a dilute alcoholic solution of sulphuric acid (ethylsulphuric acid) was added. After two days the odour of cyclobutan-1: 3-dione had disappeared. The free acid was neutralised by shaking with moist calcium carbonate, and the mixture was dried with calcium chloride, filtered, and distilled—towards the end under diminished pressure. The last fraction had the odour of acetoacetic ester, gave the characteristic violet colour with aqueous ferric chloride, and boiled at  $182^\circ/760$  mm. (corr.), pure acetoacetic ester boiling at  $181^\circ$ .

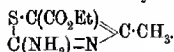
*Action of Bromine on cyclobutan-1: 3-dione:  $\gamma$ -Bromoacetoacetyl Bromide.*

In order to study the action of bromine on cyclobutan-1: 3-dione, these substances were diluted with carbon tetrachloride, which had been dried over calcium chloride and distilled. The bromine was purified by washing with aqueous potassium bromide and then with water, and distilling from phosphoric oxide. In a preliminary experiment a dilute solution of cyclobutan-1: 3-dione was titrated with a bromine solution, using the colour of the bromine as indicator. The strength of the bromine solution was found in the usual way by shaking with aqueous potassium iodide and titrating with thiosulphate. The titration of the cyclobutan-1: 3-dione was not very sharp, as towards the end the reaction became very slow, but it was sufficient to show that the substances reacted

in molecular proportions. 0.384 Gram of *cyclobutan-1:3-dione* required 0.707 gram of bromine, whilst according to the equation  $C_4H_4O_2 + Br_2 = C_4H_4O_2Br_2$ , 0.732 gram should have been used. To carry out the bromination on a larger scale, *cyclobutan-1:3-dione*, in weighed quantities of from 2 to 5 grams, was dissolved in about 50 c.c. of carbon tetrachloride contained in a 100 c.c. measuring flask. An equivalent amount of bromine, dissolved in 20 to 30 c.c. of carbon tetrachloride, was then run in very slowly from a burette, the flask meanwhile being kept immersed in cold water and well shaken. The reaction appeared to be over when a little more than 95 per cent. of the bromine had been added. The solution of the acid bromide fumed strongly on contact with moist air, and reacted vigorously with water, giving hydrobromic acid. To prepare the ester, alcohol, which had been dehydrated by means of metallic calcium, was added to the solution of the acid bromide. The substances reacted at once with evolution of heat, and the hydrogen bromide which was formed, being much less soluble in carbon tetrachloride than in the ester, "salted out" the latter, which formed a light brown layer on top of the tetrachloride. We have found that the same thing occurs if carbon disulphide is used as solvent in place of the tetrachloride. This phenomenon must have been observed in brominating ethyl acetoacetate in the ordinary way, but we have not seen it mentioned. On shaking the mixture with water, the ester at once dissolved in the carbon tetrachloride. The washing with water was continued until all free acid had been removed. The solution was then dried over calcium chloride, the carbon tetrachloride and any alcohol remaining were evaporated, and the residue was distilled under 10 mm. pressure, the bulk of the ester passing over between  $110^\circ$  and  $115^\circ$ . This is about  $15^\circ$  lower than the boiling point of the  $\gamma$ -bromoacetoacetic ester under 10 mm. pressure given by Epprecht (*Annalen*, 1894, **278**, 77); but, as this author does not state that the mercury in his manometer had been properly boiled out, the pressure in his apparatus was probably rather higher. The presence of bromine in the ester was proved by warming with dilute sodium hydroxide, sodium bromide being formed. With copper sulphate and sodium acetate, a bright green copper salt was produced. The  $\gamma$ -position of the bromine in the ester was also shown by the reaction with thiocarbamide, as described by Epprecht (*loc. cit.*), ethyl 2-aminothiazolyl-4-acetate, melting at  $93-94^\circ$ , being obtained according to the equation:



Ethyl  $\alpha$ -bromoacetoacetate would have given with thiocarbamide, ethyl 2-amino-4-methylthiazole-5-carboxylate, melting at 175°:



It is well known, however, that in certain circumstances the  $\alpha$ -bromo-ester may be converted into the  $\gamma$ -bromo-ester by the action of hydrogen bromide, and it occurred to us that this might possibly have taken place when the alcohol was added to the acid bromide. The "salting out" of the ester by the hydrogen bromide would certainly facilitate such an interchange. Accordingly, the synthesis of the ester was repeated in a slightly different way. The solution of the acid bromide was run very slowly into excess of alcohol, in which finely ground, dry sodium acetate was suspended, the mixture being kept well stirred during the process. The bromination of the cyclobutan-1:3-dione and the reaction with alcohol were both carried out at 0°. This time no "salting out" of the ester took place. The solution was washed with water, dried, and concentrated as before, but the ester was distilled under 5 mm. pressure, and passed over below 100°, leaving only a very small residue in the distilling flask. The yield of ester was about 75 per cent. of that calculated from the weight of cyclobutan-1:3-dione taken. The ester thus obtained was quite colourless. The thiazole derivative was also very nearly colourless, but it melted as before at 93° (corr.), even after repeated recrystallisation from ether.

To prepare  $\gamma$ -bromoacetoacetanilide, a little less than one molecular proportion of aniline dissolved in carbon tetrachloride was added slowly to a solution of  $\gamma$ -bromoacetoacetyl bromide in the same solvent. The anilide separated at once in the form of an almost white precipitate, which, after washing with water and drying, melted at about 134°. On recrystallising from alcohol, colourless crystals were obtained, which melted and decomposed at 138° (corr.), as given by Knorr (*Annalen*, 1886, **236**, 79) for the bromoacetoacetanilide which he obtained by brominating acetoacetanilide. The identification was confirmed by taking a mixed melting point with a sample of bromoacetoacetanilide prepared by Knorr's method. When more than one molecular proportion of aniline was added to the acid bromide, the second bromine atom was also attacked, and tarry substances were formed, from which a pure product could not be isolated. On dissolving the bromoacetoacetanilide in cold concentrated sulphuric acid, keeping the solution overnight, and then pouring into water, bromo-2-hydroxy-4-methylquinoline was precipitated, which, after recrystallising from alcohol and drying, formed the curious felt-like mass described by Knorr, which melted and decomposed at 260° (corr.). Knorr (*loc. cit.*,

p. 92) gives the melting point as "circa 258°." For comparison, a sample of bromo-2-hydroxy-4-methylquinoline was prepared by the other method described by Knorr (*loc. cit.*, p. 91). 2-Hydroxy-4-methylquinoline, obtained by digesting acetoacetanilide in the cold with concentrated sulphuric acid, was suspended in warm water, and to the mixture bromine water was added until a permanent yellow colour was produced, slightly more than one molecular proportion of bromine being required. The resulting bromo-2-hydroxy-4-methylquinoline was washed with water and recrystallised repeatedly from alcohol. In appearance it was indistinguishable, even under the microscope, from the bromohydroxy-methylquinoline prepared from bromoacetoacetanilide, but it melted, apparently without decomposing, at 273—275° (corr.), although it began to soften at 269—270°. A mixture of the two preparations melted at 240°.

The  $\gamma$ -bromoacetoacetyl bromide was evidently an unstable substance, as its solutions began to turn brown after a few hours. Nevertheless an attempt was made to isolate it in a pure state. A solution of it in carbon tetrachloride was prepared as before, starting with about 5 grams of *cyclobutan-1:3-dione*. The carbon tetrachloride was removed by distilling under diminished pressure (100 to 30 mm.), and the liquid remaining in the flask was distilled under 5 mm. pressure in a current of dry hydrogen. Between 1 and 2 grams of an oily liquid passed over between 105° and 110°, but hydrogen bromide was evolved at the same time, and a large amount of a dark-coloured residue remained in the flask. The liquid appeared colourless while on the end of the condenser tube, but was light brown when observed in the test-tubes placed to collect it. The best sample was sealed up as quickly as possible. It gradually darkened on keeping, and after a few days was nearly opaque. The other samples reacted vigorously with water, with alcohol, and with aniline, and fumed strongly in moist air. The residue in the distilling flask appeared to consist largely of free carbon. A small proportion, however, was soluble in chloroform, and the solution, when placed on the skin and washed with water, gave rise to a brilliant violet stain, which was very stable.

#### *Action of Semicarbazide on cyclobutan-1:3-dione.*

To prepare the semicarbazide derivative, *cyclobutan-1:3-dione* was treated with an aqueous solution of semicarbazide hydrochloride containing an excess of sodium acetate. A crystalline precipitate was formed on keeping, which separated from warm water in small,

rhombic (1) crystals, melting and decomposing slightly at 217–218°. The substance was insoluble in non-aqueous solvents, but was very soluble in dilute hydrochloric acid, and from this solution platinum chloride precipitated a sparingly soluble platinum chloride. Owing to the small solubility of the base in cold water, and to the fact that it was decomposed by boiling water, the molecular weight could not be determined. Analysis, however, showed that it was the semicarbazone-semicarbazide of acetoacetic acid:

0.1210 gave 0.1448 CO<sub>2</sub> and 0.0626 H<sub>2</sub>O. C=32.6; H=5.6.

0.1135 „ 0.1388 CO<sub>2</sub> „ 0.0570 H<sub>2</sub>O. C=33.4; H=5.6.

0.1106 „ 37.1 c.c. N<sub>2</sub> (dry) at 17° and 751 mm. N=39.0.

C<sub>6</sub>H<sub>12</sub>O<sub>3</sub>N<sub>6</sub> requires C=33.3; H=5.6; N=38.9 per cent.

#### *Action of Ammonia on cyclobutan-1:3-dione.*

To follow the reaction with ammonia, cyclobutan-1:3-dione in quantities of about 3 grams was dissolved in dry ether and placed in a U-tube, which was immersed in a freezing mixture of ice and salt, kept at -10° to -15°. A slow current of ammonia gas, produced by warming aqueous ammonia, and dried by passing first through a 50 per cent. solution of potassium hydroxide and then over freshly ignited lime, was then passed through the solution in the U-tube. Almost immediately a solid substance commenced to separate out; but after about twenty minutes oily drops of a yellow colour began to make their appearance. The reaction was then stopped, and the solid substance was quickly scraped on to a porous plate, which had previously been cooled to 0°. If the temperature was allowed to rise, or if the action of the ammonia was prolonged, the solid was completely converted into the yellow oil, from which it could not again be recovered. The solid substance, after drying on the porous plate, was usually pure (m. p. 54°, corr.). It was insoluble in ether, but very soluble in water, alcohol, or glacial acetic acid. It could, however, be recrystallised most conveniently from a mixture of acetone and light petroleum. The crystals were colourless. The aqueous solution gave the violet colour characteristic of acetoacetic ester. On warming with aqueous alkalis, ammonia was evolved, and if this solution was boiled with hydrochloric acid, carbon dioxide and acetone were given off, the latter being identified by the iodoform reaction, the alkaline mercuric chloride test, and the formation with benzaldehyde of distyryl ketone, melting at 112° (corr.). Heating the substance directly with hydrochloric acid caused decomposition with formation of brown compounds. On

adding ammoniacal copper sulphate to the aqueous solution of the substance and neutralising the ammonia, a green copper salt was formed:

0.1071 gave 0.1871  $\text{CO}_2$  and 0.0667  $\text{H}_2\text{O}$ .  $\text{C}=47.6$ ;  $\text{H}=6.9$ .

0.0765, in 19.59 glacial acetic acid, gave  $\Delta t = -0.157^\circ$ . M.W. = 97.

0.0798, " 19.59 " " "  $\Delta t = -0.158^\circ$ . M.W. = 101.

$\text{C}_4\text{H}_7\text{O}_2\text{N}$  requires  $\text{C}=47.5$ ;  $\text{H}=6.9$  per cent. M.W. = 101.

The substance is therefore identical with the acetoacetamide described by Claisen and Meyer (*Ber.*, 1902, **35**, 583), for which, however, they give a melting point of  $50^\circ$ . They did not determine the molecular weight.

The yellow oil formed by the further action of ammonia on acetoacetamide appears to bear some resemblance to the substance obtained by Duisberg (*Annalen*, 1882, **213**, 174) by the action of ammonia on acetoacetic ester, from which, however, this author was unable to isolate a compound having a definite composition. It is best prepared by the prolonged action of ammonia on cyclobutan-1:3-dione at  $-10^\circ$  to  $-15^\circ$ . If the reaction is started at the ordinary temperature, much heat is evolved, and coloured decomposition products are formed. The U-tube may, however, be removed from the freezing mixture as soon as all the solid acetoacetamide has disappeared. The oil thus obtained always contained excess of ammonia, which could not be completely removed, even by passing a current of dry hydrogen through it for many hours, or by leaving it over sulphuric acid in a vacuum desiccator for several months, although the pressure was sometimes reduced to 2 to 3 mm. As it was not soluble in any solvents which did not mix with water, it could not be purified by washing. It was readily soluble in water or alcohol, less readily so in acetone, and insoluble in ether, benzene, light petroleum, chloroform, or carbon tetrachloride. On exposure to moist air, a crystalline substance was formed, which, after drying on a porous plate, melted at  $147^\circ$ . A quantity of this sufficient for an analysis could not, however, be obtained. On passing a current of dry hydrogen through the yellow oil at  $110^\circ$ , ammonia and water were given off. At the end of an hour the substance had become very viscous, and a portion taken out on a glass rod solidified on cooling. The remainder was then washed out of the tube with warm acetone, and, on cooling the solution, a colourless, crystalline compound separated out, which melted at  $197^\circ$  (corr.). Recrystallisation from acetone did not alter the melting point. The compound was readily soluble in water, alcohol, or glacial acetic acid, sparingly so in cold acetone, and insoluble in ether, benzene, or light petroleum. On warming with aqueous alkalis, ammonia was evolved. For a quantitative

estimation of the ammonia, the substance was distilled with 2*N*-potassium hydroxide solution, the ammonia being caught in standard acid:

0.1133 gave 0.2176  $\text{CO}_2$  and 0.0743  $\text{H}_2\text{O}$ .  $\text{C}=52.4$ ;  $\text{H}=7.3$ .  
 0.1063 „ 21.5 c.c.  $\text{N}_2$  (moist) at  $19^\circ$  and 752.8 mm.  $\text{N}=22.9$ .  
 0.0765, in 17.75 glacial acetic acid, gave  $\Delta t = -0.092^\circ$ .  $\text{M.W.}=183$ .  
 0.0989, „ 17.75 „ „ „ „  $\Delta t = -0.128^\circ$ .  $\text{M.W.}=170$ .  
 $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_3$  requires  $\text{C}=52.5$ ;  $\text{H}=7.1$ ;  $\text{N}=22.9$  per cent.  
 $\text{M.W.}=183$ .

0.2369 gave 0.0233  $\text{NH}_3$ , that is, 183 grams  $\text{C}_8\text{H}_{13}\text{O}_2\text{N}_3$  gave 18.0 grams  $\text{NH}_3$ .

As stated on p. 1982, we consider the substance to be 4-amino-2:4-dimethyl- $\Delta^2$ -tetrahydro-6-pyridone-3-carboxylamide, 183 grams of which should give 17 grams of ammonia on distilling with dilute alkalis. On acidifying the alkaline solution from which the ammonia had been distilled with nitric acid, the free 4-amino-2:4-dimethyl- $\Delta^2$ -tetrahydro-6-pyridone-3-carboxylic acid was not precipitated, but the silver and barium salts appeared to be insoluble in water. We propose to prepare larger quantities of the amide from acetoaceta<sup>1</sup>ride obtained by Claisen and Meyer's method (*loc. cit.*).

#### *Action of Grignard's Reagent on cyclobutan-1:3-dione.*

To study the action of Grignard's reagent (magnesium methyl iodide), from 3 to 4 grams of cyclobutan-1:3-dione were dissolved in about 50 c.c. of dry ether contained in a large test-tube, and rather more than two molecular proportions of the reagent, dissolved in about 100 c.c. of ether, were placed in a second tube of about 200 c.c. capacity. The reagent was kept at  $-78^\circ$  by means of a bath of solid carbon dioxide and alcohol, and the solution of cyclobutan-1:3-dione was cooled to about  $-50^\circ$ , a lower temperature than this causing the solute to crystallise out. The reagent was kept vigorously stirred by means of a current of air dried over phosphoric oxide, and the solution of cyclobutan-1:3-dione was run in very slowly in a fine stream by means of a wash-bottle arrangement, dry air under pressure being used to drive the liquid over. Even at the low temperature of  $-78^\circ$ , a bright yellow precipitate was at once formed. On allowing the temperature to rise, the precipitate turned brownish-red at about  $-40^\circ$ , and became almost black above  $0^\circ$ . In this condition only resinous substances appeared to be formed when the mixture was run into ice-water. It was found preferable to add the ethereal mixture slowly, as soon as it had reached  $-40^\circ$  to  $-30^\circ$ , to a 2*N*-sulphuric acid solution, containing a slight excess of acid, which



was kept partly frozen during the mixing by a freezing mixture. At the end of the reaction, the ethereal solution was separated, and the aqueous solution was shaken with fresh ether, which was added to the first. The ethereal solution was dried over calcium chloride and distilled, the pressure being reduced to 50–60 mm. after the ether had been removed. A small amount of liquid passed over at 80–100°, and a few drops of a bright yellow liquid, having a pleasant aromatic odour, at 180–200°. The last portion of this yellow liquid solidified in the condenser tube on cooling to yellow needles, which, after drying on a porous plate, melted at 145–146°. On adding water to the yellow liquid, more of the yellow solid was precipitated, leaving a nearly colourless solution. This was extracted with ether, the ethereal solution dried with calcium chloride, and evaporated, when a small quantity of a high boiling liquid remained. This gave an orange-coloured solution with concentrated sulphuric acid, and, on pouring this into water, a small quantity of an oil was formed, which had an odour resembling that of mesityl oxide. The fraction of the lower boiling point also had an odour resembling that of mesityl oxide, and it gave a bright red colour with concentrated sulphuric acid. A considerable amount of residue remained in the distilling flask, and resinous substances were also formed on neutralising and evaporating the aqueous solution.

Owing to the poor yield, it was not possible to obtain a liquid having a definite boiling point. It is, however, probable from the foregoing that the reaction proceeds, at any rate to a small extent, in the direction indicated on p. 1983. It is evident that some of the intermediate compounds, possibly including the compound formed when only one CO group has been attacked, are very unstable, readily condensing to form resinous substances.

#### *Reduction of cycloButan-1:3-dione.*

This reduction promised to be of interest, but the choice of means was limited. On account of the chemical nature of the substance, the more usual reducing agents were inadmissible, and, owing to the tendency to polymerise on heating, Sabatier and Senderens' method was not promising. Accordingly, the method of reduction by means of hydrogen and platinum black was selected.

The hydrogen was prepared from zinc and dilute sulphuric acid, which were free from arsenic. The gas was passed through a tube packed with copper gauze and kept at a red heat to absorb traces of oxygen, which would otherwise have been reduced to water in contact with the platinum black, and it was dried by means of sulphuric acid contained in a spiral wash-bottle. The platinum

black was prepared by Loew's method (*Ber.*, 1890, 23, 289). It was washed until free from chlorides, and was dried in a vacuum over sulphuric acid. The reduction vessel consisted of a large test-tube fitted with a rubber stopper, through which passed inlet and outlet tubes for the hydrogen and a tap funnel. The inlet tube reached to the bottom of the reduction vessel. About 2 grams of platinum black were placed in the reduction tube, and the air in the latter was replaced by hydrogen. The platinum black was then again dried by warming the tube to about 60°, and alternately exhausting with a Fleuss pump and filling with hydrogen. About 4 grams of *cyclobutan-1:3-dione*, dissolved in dry ether, were then introduced through the tap funnel, and a slow current of hydrogen was turned on, the lower end of the reaction vessel being placed in a water-bath to prevent cooling during the evaporation of the ether. After about two hours, most of the ether had been driven off, and a spiral condenser fitted with taps, such as was used for collecting keten, was attached to the outlet tube, and was surrounded by a bath of solid carbon dioxide and alcohol, in order to catch any volatile compounds which might otherwise be carried away by the hydrogen. The water-bath was now warmed to about 65°, and was maintained at that temperature by means of an electric heater. After two days the odour of *cyclobutan-1:3-dione* could no longer be detected at the outlet tube of the reduction vessel on detaching the condenser, but a strong odour of butyric acid became noticeable when the connecting tubes were opened to the air. The reduction vessel was then completely immersed in the water-bath, and the temperature was raised to about 95°. After a further twelve hours, all the liquid had passed over into the condenser, which was found to contain a white, crystalline solid. A small quantity of a brown residue remained with the platinum. In order to ascertain whether any compounds had been formed which were gaseous at the ordinary temperature, the condenser was attached to a manometer and to the Fleuss pump and exhausted to about 5 mm. pressure. The tap leading to the pump was then closed, and the temperature was allowed to rise. The solid melted at about -20°, but the pressure did not rise above 50 mm., even when the apparatus had attained the temperature of the room. The condenser was then filled with dry air, after which it had to be set aside for a few days. On again opening the taps, it was noticed that a reduction of pressure had taken place, indicating absorption of oxygen. On transferring the contents of the condenser to a distilling flask and distilling, the major portion passed over at 70-80°, and on reducing the pressure to 20 mm., a further portion passed over at about 80°. The first fraction had an odour

resembling that of acetaldehyde, but, on exposure to air, a strong odour of butyric acid was developed. This fraction also gave pronounced aldehyde reactions. The fraction of higher boiling point had a strong odour of butyric acid. It was readily soluble in water, was acid to litmus, and liberated carbon dioxide from sodium carbonate with formation of a very soluble crystallisable salt. It boiled at  $163\text{--}164^{\circ}/757\text{ mm. (corr.)}$ , and, after solidifying in a freezing mixture, it melted at  $-7^{\circ}$  to  $-6^{\circ}$ . The substance was therefore *n*-butyric acid, formed by the oxidation in air of the aldehyde. *n*-Butyraldehyde was accordingly the final product of the reduction of *cyclobutan-1:3-dione* by the method employed. The intermediate stages of the reaction are suggested on p. 1983. The water formed would, of course, combine with excess of *cyclobutan-1:3-dione* to form acetoacetic acid, which, at the temperature of the experiment, would decompose into carbon dioxide and acetone. It was anticipated, from analogy to the reduction of acetoacetic ester with sodium amalgam, that aldol or  $\alpha$ - $\gamma$ -dihydroxybutane might have been formed, but no trace of these could be detected.

#### *Condensation of cyclobutan-1:3-dione.*

In our former paper we stated that "acetylketen" slowly turned brown on keeping at the ordinary temperature, and that brown resins were formed when it was distilled under the atmospheric pressure. We have since found that when *cyclobutan-1:3-dione* is heated in sealed tubes on a water-bath to  $80\text{--}90^{\circ}$ , it is converted chiefly into dehydracetic acid, the reaction being complete after two to three hours. A certain amount of brown resins and of carbon dioxide are, however, formed at the same time. Also, in some samples, which had been sealed up in glass tubes and kept at the ordinary temperature, crystals of dehydracetic acid made their appearance after several weeks; but here again brown resins and carbon dioxide were also produced. The yield of dehydracetic acid was, however, the greater the lower the temperature at which condensation took place. Condensation did not appear to be accelerated by the action of light, for a sample of *cyclobutan-1:3-dione*, which had been sealed up in a bulb of "uviolet" glass and exposed to bright sunlight, did not turn brown more rapidly than other samples kept in the dark at the same temperature. On the other hand, *cyclobutan-1:3-dione* is the more stable the lower the temperature at which it has been distilled. From the formation of brown resins and of carbon dioxide along with the dehydracetic acid, it is evident that the condensation follows more than one course.

On account of the manifold reactions of the multiple keten

groups, for the study of which dehydracetic acid has been the chief starting point, notably in the hands of Collie and his pupils (compare Trans., 1907, **91**, 1806), the proof of the formation of this compound from *cyclobutan-1:3-dione*, and consequently from keten itself, was of special importance. After recrystallisation, the dehydracetic acid melted at  $109^{\circ}$  (corr.), and the melting point was not altered by mixing with a sample of pure dehydracetic acid from other sources. Under the microscope the two samples appeared to be identical when they had been crystallised in the same way. The dehydracetic acid from *cyclobutan-1:3-dione* also gave an orange colour with ferric chloride. Finally, it was converted by the usual method into diacetylacetone, which was identified by the yellow barium salt and the characteristic violet colour with ferric chloride.

*Condensation of cyclobutan-1:3-dione in Presence of Quinoline.*

The condensation of *cyclobutan-1:3-dione* in the presence of quinoline has also been further investigated. Quantities of about 5 grams of *cyclobutan-1:3-dione* were mixed with an approximately equal amount of pure quinoline in a wide test-tube, to which was fitted a rubber stopper and a mercury valve to allow of the escape of gas and at the same time to exclude air. After two or three days yellow crystals appeared in the tube, and the supernatant liquid became dark brown, while carbon dioxide was slowly given off. After ten days to a fortnight the reaction appeared to be complete, and the contents of the tube, now become very viscous, were scraped out into a mortar and ground up with acetone, in which the yellow crystals were not soluble. The yellow substance was then collected and washed thoroughly with acetone, after which it was dissolved in hot glacial acetic acid and reprecipitated by the addition of water. It was usually pure after one such recrystallisation, melting at  $244^{\circ}$  (corr.). (In our former paper we gave  $231^{\circ}$  as the melting point, but the substance then available was not quite pure.) The yield was not good, being only about 20 per cent. of the weight of *cyclobutan-1:3-dione* taken, and this was much reduced if impure quinoline had been used. The acetone filtrate from the yellow compound was dark reddish-brown when viewed by transmitted light, and had a marked green fluorescence by reflected light. It contained only resinous substances, from which a pure compound could not be isolated.

It was difficult to obtain satisfactorily consistent analytical numbers, probably owing to the formation of methane on heating:

0.0848 g. gave 0.2258  $\text{CO}_2$  and 0.0367  $\text{H}_2\text{O}$ .  $\text{C}=72.6$ ;  $\text{H}=4.8$ .

0.1100 " 0.2931  $\text{CO}_2$  " 0.0468  $\text{H}_2\text{O}$ .  $\text{C}=72.7$ ;  $\text{H}=4.7$ .

0.0683, in 18.94 glacial acetic acid, gave  $\Delta t = -0.066^\circ$ . M.W. = 213.  
 0.0693, " 17.63 " " " "  $\Delta t = -0.068^\circ$ . M.W. = 225.  
 0.0531, " 17.85 " " " "  $E = 0.032$ . M.W. = 235.  
 $C_{13}H_{10}O_3$  requires C = 72.9; H = 4.7 per cent. M.W. = 214.

The substance was readily soluble in hot glacial acetic acid, but much less so in the cold acid, crystallising on cooling in bright yellow needles or plates. The solutions were bright yellow, with a green fluorescence. It was slightly soluble in benzene, almost insoluble in alcohol or acetone, and insoluble in water, chloroform, light petroleum, or ether. It was soluble in dilute alcoholic potash, forming a red solution from which it could be reprecipitated in a somewhat impure form by hydrochloric acid. A suspension of the substance in water was neutral to litmus, but addition of ferric chloride gave a red colour, which was not discharged by dilute hydrochloric acid. It was insoluble in aqueous alkalis, and it did not react with benzoyl chloride, so that hydroxyl groups would appear to be absent. It dissolved on warming with 75 per cent. sulphuric acid, forming a deep yellow solution with a green fluorescence, but the original substance could not be recovered by neutralising the acid. Some reaction had therefore taken place, probably the removal of a side chain.

As the yellow compound had a strong resemblance to certain naphthalene derivatives discovered by Collie (Trans., 1893, 63, 329; 1896, 69, 293), an attempt was made to prepare the parent hydrocarbon. Owing to the small quantity of material available, distillation with zinc dust did not offer much prospect of success, and electrolytic reduction was therefore tried. The solution of the substance in sulphuric acid was diluted until the strength of the acid was about 25 per cent., and was placed in a porous pot, together with a cathode of platinum gauze, which could be rapidly rotated. To prevent formation of oxidising substances, an amalgamated zinc plate was used for the anode, a slow stream of 25 per cent. sulphuric acid being made to flow through the anode vessel to remove the bulk of the zinc which dissolved. The current density was about 0.1 ampere per sq. cm. After electrolysis had proceeded for some hours, the cathode solution was shaken with benzene, and, on evaporation of the latter, a minute quantity of a colourless substance, melting at  $96-97^\circ$ , was obtained. The yield could not be improved. Substitution of a zinc cathode for the platinum gave only oily substances, which could not be caused to crystallise, and which were too small in quantity for effective distillation.

A suspension of the substance in carbon tetrachloride decolourised a solution of bromine in the same solvent. A crystalline substance appeared to be formed at first, but it dissolved on further addition

of bromine. On shaking the mixture with water, hydrobromic acid could be detected in the latter. In the quantitative experiments weighed quantities of the substance were shaken with a moderate excess of bromine solution, and, when the substance had completely dissolved, the excess of bromine was determined by means of potassium iodide and thiosulphate in the usual way. The free acid was then found by titration with standard alkali. The bromine solution contained 0.0275 gram equivalent per litre and the alkali 0.0384 equivalent:

0.0707 gram required 25.64 c.c. bromine solution and 15.99 c.c. alkali.

Or 214 grams reacted with 2.13 equivalents of bromine, forming 1.86 equivalents of acid.

0.0757 gram required 26.37 c.c. bromine and 16.68 c.c. alkali.

Or 214 grams reacted with 2.05 equivalents of bromine, forming 1.81 equivalents of acid.

The formation of nearly two equivalents of acid from two equivalents of bromine would seem to indicate the formation of an acid bromide, as in the reaction between bromine and keten (Trans., 1907, 91, 1941), or in that between bromine and *cyclobutan-1:3-dione* described above, this acid bromide on addition of water giving one equivalent of hydrobromic acid and one of another acid.

The yellow compound was attacked by dilute permanganate in the cold, but only acetic acid could be detected among the products of oxidation. It also reacted with phenylhydrazine in glacial acetic acid, forming a compound containing nitrogen, which was insoluble in benzene but very soluble in alcohol, from which it could be crystallised in colourless needles or plates, melting sharply at 238°. A quantity sufficient for analysis could, however, not be obtained.

On treatment with an alkaline solution of hydroxylamine, an oxime was formed. The yellow compound was dissolved in a solution containing 10 grams of potassium hydroxide to 20 c.c. of water with 120 c.c. of alcohol. Excess of hydroxylamine hydrochloride dissolved in a little water was added, and the mixture was warmed for five minutes on the water-bath. On neutralising with hydrochloric acid, a yellow substance slowly separated, precipitation being complete in about two hours. It was washed with water and recrystallised from hot water. It was also soluble in alcohol. It melted and decomposed at 200° (corr.). The results of analysis seem to show that we did not succeed in getting this substance in a completely pure state; in fact, it could not be dissolved without showing signs of decomposition:

0.1072 gave 0.2336  $\text{CO}_2$  and 0.0576  $\text{H}_2\text{O}$ .  $\text{C}=59.4$ ;  $\text{H}=6.0$ .

0.1030 „ 0.2342  $\text{CO}_2$  „ 0.0517  $\text{H}_2\text{O}$ .  $\text{C}=61.5$ ;  $\text{H}=5.6$ .

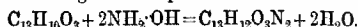
0.1084 „ 0.2436  $\text{CO}_2$  „ 0.0555  $\text{H}_2\text{O}$ .  $\text{C}=61.3$ ;  $\text{H}=5.7$ .

0.1126 „ 9.98 c.c.  $\text{N}_2$  (moist) at  $18.5^\circ$  and 761.6 mm.  $\text{N}=10.2$ .

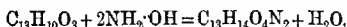
I.  $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$  requires  $\text{C}=63.9$ ;  $\text{H}=4.9$ ;  $\text{N}=11.5$  per cent.

II.  $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}_2$  „  $\text{C}=59.5$ ;  $\text{H}=5.3$ ;  $\text{N}=10.7$  „

Formula I results from the reaction of hydroxylamine with two  $\text{:CO}$  groups according to the equation:



Formula II represents the reaction of two molecules of hydroxylamine,\* one reacting normally with a  $\text{:CO}$  group, and the other adding on to a double bond:



The aqueous solution of the hydroxylamine compound was acid to litmus. It was titrated with standard alkali containing 0.0384 equivalent per litre:

0.0777 gram required 6.23 c.c. alkali.

That is, 244 grams  $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$  require 0.75 equivalent of alkali, and 262 grams  $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}_2$  require 0.81 equivalent of alkali.

It will be seen from the foregoing that so far we have found no clue to the constitution of the yellow condensation product of *cyclobutan-1:3-dione*, and the yield in the preparation of the substance and of all its derivatives is so poor that very much larger quantities of the raw material (that is, of *cyclobutan-1:3-dione*) than have been hitherto available would be required before this portion of the research could be resumed with any chance of success.

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## CCXI.—The Viscosity of Salt Solutions.

By MALCOLM PERCIVAL APPLEBEY.

THE changes in viscosity produced when salts are dissolved in water have been the subject of many important researches since Poiseuille's classical work on the flow of liquids in capillary tubes. The results obtained by the earlier workers in this field may be summarised as follows:

(1) The effect of salts on the viscosity of water is small, but generally positive. Some salts, however (for example, potassium chloride), diminish the viscosity of water.

(2) The effect of salts in increasing the viscosity increases more

rapidly than the concentration; the salts which diminish the viscosity have, however, less effect as concentration increases. A minimum value is reached at a certain concentration. The addition of more salt then raises the viscosity.

(3) The effect of a salt in increasing the viscosity of water is additively composed of a factor expressing the effect of the cation and a factor expressing the effect of the anion, when the solution is sufficiently dilute.

(4) The temperature-coefficient of the viscosity of a dilute salt solution is approximately equal to that of water.

These researches were necessarily confined to concentrated solutions, since the methods used were not of sufficient accuracy to measure the small changes in viscosity produced by small quantities of dissolved salt. It should also be noted that the earlier work is vitiated by the fact that the authors did not investigate the behaviour of their apparatus with respect to Poiseuille's law, but always, assumed its rigid validity. The velocity of flow in the viscometers used was always greater than the limiting velocity at which eddying begins, and above which Poiseuille's law is not rigidly obeyed. The error thus caused in the determinations cannot be calculated from the data given.

Within recent years attention has been directed to the phenomena of viscosity in dilute solutions. The work of Kohlrausch (*Proc. Roy. Soc.*, 1903, **71**, 338) and that of Bousfield and Lowry (*Phil. Trans.*, 1905, **204**, A, 253) has shown the importance of studying changes of viscosity for the interpretation of the results obtained in conductivity determinations. The application of Stokes' theorem to strong electrolytes has made the knowledge of the viscosity effect of salts in dilute solution of great importance in the measurement of ionisation and the application of the dilution law to these solutions. The advance in the accuracy of relative viscosity determinations necessary for the investigation of these problems was secured by the important work of Grüneisen (*Wiss. Abh. Phys.-Tech. Reichs.*, 1905, **4**, 151). The theory of the viscometer was very thoroughly investigated by him, and methods of standardisation were developed which enabled him to determine the deviation of any viscometer used from the simple Poiseuille law. His experiments were all corrected for this deviation, and furnish the first accurate determinations of viscosity in dilute solutions.

Investigations have also been carried out by Hosking (*Phil. Mag.*, 1904, [vi], **7**, 469), who has studied the effect of temperature and concentration over wide limits for lithium chloride, whilst Bousfield and Lowry (*Phil. Trans.*, 1906, **206**, A, 101) have also made some observations on dilute solutions.



The work of Grüneisen is remarkable for the discovery of a general phenomenon which the less exact methods of earlier workers had not revealed. He has shown that the viscosity-concentration curve for all salts has a change of curvature at the dilute end in the sense that the first particles of salt added to water have a greater effect in increasing, or a less effect in diminishing, the viscosity of water than subsequent additions. The change of curvature is scarcely noticeable unless the curve is plotted on a very large scale. A much more convenient method is to plot the differential quantity:

$$\frac{\text{Relative viscosity} - 1}{\text{Molecular concentration}}$$

against the cube-root of the concentration as recommended by Grüneisen.

This change of curvature was observed by Grüneisen with every member of a large series of salts investigated by him. No such effect has ever been found in solutions of non-electrolytes. It is not surprising therefore that Grüneisen has endeavoured to connect the phenomenon with ionisation. The following formula given by him corresponds with the observations with fair accuracy over a considerable range:

$$\frac{\eta/\eta_0 - 1}{m} = Aa + B(1 - a) + Cm,$$

where  $\eta/\eta_0$  = relative viscosity,  
 $m$  = molecular concentration,  
 $a$  = degree of ionisation,  
 and  $A$ ,  $B$ , and  $C$  are constants.

The present work was undertaken with the following objects:

- (1) To carry the investigations to greater dilutions than Grüneisen reached, and thus to test his formula;
- (2) To determine the effect of temperature, especially in dilute solutions; and
- (3) To investigate the connexion between the viscosity of a solution and its molecular and ionic conditions.

*Materials.*—It was thought advisable to investigate thoroughly some one salt over wide ranges of temperature and concentration. Lithium nitrate was chosen, as its high solubility permits the investigations to be carried to very high concentrations. It was obtained either from Kahlbaum or from Merck in the form of crystalline lumps with an indefinite amount of water of crystallisation. It appeared to be a mixture of the two hydrates,  $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ , described by Donnan and Burt (Trans., 1903, 83, 335). It was recrystallised before use in the form of the trihydrate. A spectroscopic examination showed no

impurities except a trace of sodium. The water used was conductivity water free from dust. The dissolved air was removed by exhaustion in the cold just before use. This precaution is necessary to prevent the appearance of air-bubbles in the apparatus during determinations.

*Preparation of Solutions.*—The anhydrous salt is extremely hygroscopic, and very prolonged heating is necessary to bring it to a constant weight. The making up of solutions by weight is thus a very tedious process. It was therefore decided to determine the concentration of the solutions used by means of a previously determined density curve at  $25^{\circ}$ . The dehydration of the salt for this purpose did not present such difficulties, as less of the salt was necessary for a determination. The labour was also much lessened by the use of a specimen crystallised at about  $70^{\circ}$ , which was practically anhydrous. An appropriate weight of the salt was dehydrated by heating it for at least twenty-four hours in a small platinum crucible in an air-bath heated by boiling aniline. The crucible was allowed to cool in a desiccator, and then weighed in a stoppered glass bottle. The correct weight of water was then weighed into a wide-mouthed stoppered bottle, and the crucible dropped in.

*Density Determinations.*—The determinations at  $25^{\circ}$  and  $18^{\circ}$  were made in U-shaped pyknometers of test-tube glass, holding about 10 c.c. Each pyknometer was weighed against a counterpoise, and the results were corrected for displaced air. The density of each solution was determined with two separate pyknometers.

On account of the expansion of the solution before weighing, these pyknometers could not be used at  $0^{\circ}$ . The form shown in Fig. 1 was used for this temperature. The pyknometers used held about 20 c.c. The results usually agreed to 0.00002, although the agreement was not always so good at  $0^{\circ}$ . This is due, in part, to the difficulty of temperature regulation, and in part to the contamination of the ground surface, in which the stopper fits, with solution in some experiments. Simple wiping with a filter-paper (the usual method of cleaning the open end of a pyknometer) fails to remove this. The error might have been avoided if the stopper had been ground on outside instead of inside the open end of the pyknometer. For the purpose of viscosity determinations, however,

FIG. 1.



an accuracy of 0.0001 is amply sufficient at 0°, and the errors were never so large as this.

The densities determined at 25.01° are given in table I. The following equation was found to express the results with sufficient exactness to justify its use for calculating concentrations:

$$m = 25.103 (s - s_0) - 16.337 (s - s_0)^2,$$

where  $s$  = density of solution,

$s_0$  = density of water,

$m$  = concentration expressed in gram-molecules per 1000 grams of solution.

The degree of accuracy obtained in determining concentrations in this manner may be seen by the second column of table I.

TABLE I.—*Density of solutions of lithium nitrate at 25.01°.*

Concentration. Concentration, from equation.	Concentration calculated	Dens. Pyknometer		Mean density.
		I.	II.	
0.0	0.0	—	—	0.99707
0.1286	0.1296	1.00225	—	1.00225
0.1378	0.1388	1.00262	1.00263	1.00262
0.1458	0.1463	1.00293	1.00291	1.00292
0.1571	0.1577	1.00338	1.00338	1.00338
0.1724	0.1722	1.00396	—	1.00396
0.1971	0.1981	1.00500	1.00500	1.00500
0.2137	0.2144	1.00565	1.00567	1.00566
0.3145	0.3137	1.00967	1.00970	1.00969
0.3255	0.3238	1.01008	1.01008	1.01008
0.3605	0.3606	1.01158	1.01155	1.01157
0.3905	0.3899	1.01275	1.01277	1.01276
*0.4248	0.4016	1.01325	1.01325	1.01325
0.4851	0.4855	1.01664	1.01668	1.01666
0.0068	0.0061	1.02160	1.02163	1.02161
0.8283	0.8281	1.03077	1.03082	1.03080
0.9059	0.9050	1.03400	1.03402	1.03401
*0.9960	0.9861	1.03741	1.03741	1.03741
1.0968	1.0960	1.04206	1.04205	1.04205
1.2763	1.2752	1.04967	1.04967	1.04967
1.8639	1.8633	1.07529	1.07527	1.07529
2.2027	2.2020	1.09047	1.09047	1.09047
2.4602	2.4591	1.10223	—	1.10223
3.4086	3.4083	1.14759	1.14759	1.14759
*5.876	5.849	1.28344	1.28340	1.28342

The three solutions marked with asterisks show divergences considerably greater than the errors in determining the increase in density. In all three cases the concentrations calculated from the densities are smaller than those calculated from the weighings. It is most probable that the salt used in these experiments was not fully dehydrated. These values have been omitted in calculating the constants of the equation.

The densities at 18° and 0° are given in tables V and VI. The

values at 18° agree very well with those determined by Kohlrausch and used by Grüneisen. The density determined by Perkin (Trans., 1893, 63, 68) for a 2.63 weight-normal solution (=18.17 per cent.) at 25° is, however, considerably higher than that read off my curve.

*Viscosity Determinations.*—The use of viscometers of the Ostwald type in the measurement of relative viscosity depends on the validity of the law of Poiseuille, which is expressed by the equation:

$$\eta = \frac{\pi p r^4 t}{8 l V},$$

where  $\eta$  is the coefficient of absolute viscosity,

$p$  is the mean pressure producing flow,

$V$  is the volume of liquid which flows through the capillary in the time  $t$ ,

$r$  is the radius, and

$l$  the length of the capillary.

Since  $r$ ,  $l$ , and  $V$  are constants depending only on the dimensions of the viscometer, the relation:

$$\eta = pt \times \text{constant}$$

should hold good for different liquids in the same viscometer, and if experiments are carried out with the same liquid flowing under different pressures, the product  $pt$  will have a constant value when the viscometer obeys Poiseuille's law.

Grüneisen (*loc. cit.*) has shown that this condition is by no means rigidly fulfilled by viscometers of the Ostwald type acting under their own hydrostatic pressure. He has found that the variation of  $pt$  is due to the fact that above a certain limiting velocity the flow of liquid in the viscometer is not steady, but that some of the potential energy is expended in forming eddies within the liquid. Hence the liquid is not forced down the capillary so quickly as it should be if Poiseuille's law held good, that is,  $t$  is greater than demanded by the simple law, and in consequence  $pt$  has a greater value than the constant found with slow flow.

Thus the phenomena of flow under varying pressures may be summarised as follows. When the pressure is small and the time large,  $pt$  is constant; on increasing the pressure and diminishing the time, a point is reached where eddy-formation begins. Beyond this point  $pt$  continually increases, and Poiseuille's law no longer holds. The readings of a viscometer are only trustworthy when the time of flow is so large as to ensure that the product  $pt$  remains constant (for the same liquid) over the whole range of variation in time of flow to be observed in the actual determinations. Grüneisen has tested several viscometers in a manner similar to that to be described later, and has published (*loc. cit.*) the  $pt$ - $t$  curves

obtained. He then calculated a correction for the variation in  $\eta$  over the region of his experiments, and applied this throughout his work.

It was thought possible to construct viscometers in which this correction should be negligible by reducing the velocity of flow considerably below the limits attained by Grüneisen.

This diminution in velocity of flow may be secured in three distinct ways:

- (a) By reducing the diameter of the capillary.
- (b) By lengthening the capillary.
- (c) By reducing the hydrostatic pressure in the viscometer by bringing the two bulbs as near together as possible.

(a) Some experiments were tried with viscometers constructed with very fine capillaries. It was found, however, that the results were almost invariably vitiated by dust. The final form of viscometer adopted had a capillary radius of about 0.2 mm.; thus my tubes were considerably smaller than Grüneisen's, the radius of which varied between 0.34 and 0.48 mm.

(b) and (c) To lengthen the capillary in the ordinary Ostwald type of viscometer is to increase the pressure proportionally. The form shown in Fig. 2 was therefore adopted.\* The bulbs cannot be brought nearer together than a certain limiting distance depending on the capillary rise in the viscometer; otherwise the liquid never falls below the lower mark. In the viscometers used, the lower mark was etched very near to the bulb where the capillary was slightly enlarged. At the completion of the experiment, the meniscus came to rest a few millimetres below the mark. The dimensions of the viscometers finally adopted were:

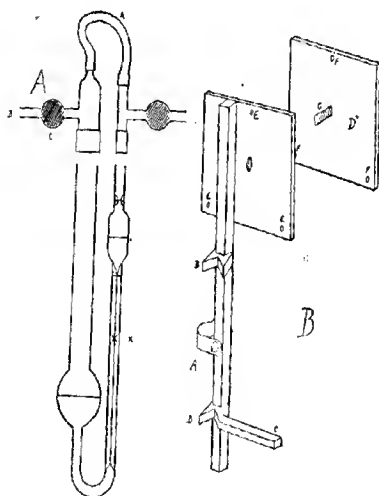
Radius of capillary .....	0.2 mm.
Length of capillary .....	11 to 22 cm.
Volume of bulb .....	7 c.c. (approx.).
Mean difference of level .....	10.8 cm. (approx.).

How far the results given by any particular viscometer are vitiated by eddy-formation also depends on the amount of irregularity in the capillary (and especially at the ends of the capillary, where the flow suddenly changes). In the construction of a viscometer anything approaching a sudden change of diameter should be avoided. The junction of capillary and bulb should have the form of a smooth cone, as shown in Fig. 2.

\* The same object has been attained by Grüneisen by winding the capillary in a spiral. This method is, however, open to the objection that much of the energy which should be expended in driving the liquid on is used in changing the direction of flow as the capillary bends. This results in a very high value for the Grüneisen eddy-correction. Since it was hoped to avoid the Grüneisen correction altogether no experiments have been performed with spiral capillaries.

*Standardisation of Viscometers.*—Although from the dimensions of the viscometers it was probable that Poiseuille's law would be obeyed within the limits of experimental error, it was necessary to carry out special tests so as to be certain that irregularities in the glass were not present of such magnitude as to produce eddies and thereby cause the viscometers to disobey the simple law. The method here described is similar to that used by Grüneisen. In order to test a viscometer, it is necessary to observe its time of flow under varying pressures when filled with water, and to investigate the variation of the product  $pt$ . The pressure in any

FIG. 2.



particular experiment is the sum of the external pressure applied and the hydrostatic pressure due to the head of liquid in the viscometer. The latter varies during the experiment, and an average value has to be found in the following way.

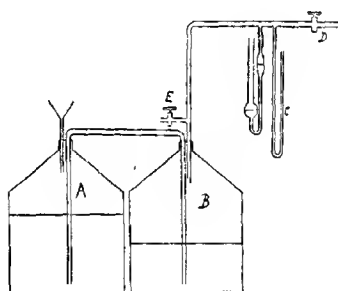
First, the small arm of the viscometer is attached to a water manometer, and the pressure directly read off by means of a reading-telescope and scale, together with the level at which the water stands in the viscometer. This determination is repeated for several different positions of the liquid in the viscometer, and a curve is drawn representing the variation in pressure head as the

liquid falls in the viscometer. Secondly, by means of the reading-telescope, the time necessary for flow from the upper mark to known distances below the mark is measured. By combining these curves, namely, variation of pressure with depth and variation of time with depth, a curve is drawn which shows the variation of pressure with time throughout the whole tube. From this a value is obtained for the average hydrostatic pressure during flow. This is usually approximately equal to the pressure at mean time, but differs from that calculated from the difference of level at mean time owing to surface effects; for example, in one viscometer:

Mean hydrostatic pressure .....	10.69 cm. of water at 25°
Pressure at mean time .....	10.55 " " "
Difference of level at mean time...	10.99 " " "

The difference between the first and third of these numbers measures the surface-tension effect, and will be considered later.

FIG. 3.



The times of flow have now to be measured when a known excess of pressure is applied at the small arm of the viscometer. For this purpose it is necessary to have an arrangement capable of exerting a small pressure, which shall keep quite constant during the experiment. I have found the apparatus shown in Fig. 3 to work very satisfactorily. The vessels *A* and *B*, which contained water, were so large that the movement of the air into the bulb of the viscometer during flow made no measurable alteration in the difference of level in *A* and *B* measured by the water manometer *C*. The pressure of the air in *B* remained constant to 0.1 mm. of water during the experiment when the cork of *B* and the rubber connexions were painted with celluloid varnish so as to prevent leakage. The pressure in *B* can be varied by allowing air to escape from *D* or by forcing in air with a bicycle-pump at *E*. The range

for pressures under which experiments were performed was  $-1$  to  $+20$  cm. of water. The pressures were measured on the water manometer *C*, which could be read to  $0.1$  mm. by a reading-telescope.

The following table gives the values obtained with a satisfactory tube:

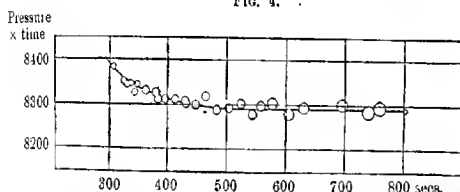
TABLE II.

Viscometer *R*. Hydrostatic pressure =  $10.36$  cm. of water at  $25^{\circ}$ .

Total pressure.	Time of flow in secs.	Pt.	Total pressure.	Time of flow in secs.	Pt.
10.26	800.2	8290	19.19	432.6	8302
10.94	758.4	8297	19.26	431.4	8309
11.205	739.5	8286	20.09	413.7	8311
11.93	695.8	8301	20.96	396.5	8311
13.15	630.8	8295	21.61	384.6	8311
13.69	605.0	8282	21.865	380.8	8326
14.33	577.5	8304	22.89	363.9	8350
14.85	558.8	8298	23.94	348.5	8343
15.23	543.6	8279	24.20	344.0	8325
15.83	524.6	8304	24.75	337.2	8346
16.47	503.6	8294	25.20	331.1	8344
17.14	483.6	8289	25.68	325.2	8351
17.85	466.0	8318	25.94	321.7	8345
18.64	447.6	8299	27.27	307.4	8383

These values are plotted in Fig. 4; the radius of the circles represents the experimental error of the determinations. The

FIG. 4.



values of  $pt$ , although varying considerably, do not, at low pressures, differ by more than the experimental error. At higher pressures,  $pt$  rises above its normal value, the increase becoming rapid as the pressure increases. The experimental error in standardising is unfortunately much greater than that of the viscosity determinations. It is thus not quite certain that the tube obeys Poiseuille's law with the necessary accuracy. The following facts, however, indicate that the assumption is justifiable:

(1) Within the attainable limits of accuracy of standardisation no deviation from Poiseuille's law can be detected until the time of flow falls well below the minimum time of flow in the actual determinations.



(2) The times of flow of any pair of tubes filled with water were in the same ratio as the times of flow for any solution determined. This shows that either the tubes obey the law rigidly, or that they all deviate to the same extent.

(3) The velocity of flow in the capillaries of my viscometer is only about one-fifth of that prevailing in Grüneisen's experiments. The correction applied by him for deviation from Poiseuille's law is only 0.045 per cent. for a normal solution of lithium nitrate. It is therefore probable that the deviation of my tubes from Poiseuille's law is not more than 0.01 per cent., and is consequently negligible for solutions less concentrated than normal.

*Time.*—This was measured by means of a carefully tested stop-watch, which was always in a constant state as regards winding at the beginning of each determination (the watch was always wound to its fullest extent half an hour before filling the viscometer). In the later experiments an electromagnetic device was used to start and stop the watch. The error in time determinations with a stop-watch is not greater than 0.2 sec., and with a large number of determinations the error of the mean result is not more than 0.1 sec. This is an error of 1 in 8000 at its maximum. In view of the magnitude of the other errors of the determinations, particularly the temperature effect, since with water a difference of  $0.005^{\circ}$  at  $18^{\circ}$  produces a change of 0.2 sec. in the time of flow of the quickest tube used, it seemed useless to attempt any more accurate determination of time.

*Cleaning.*—As the deposition of the least particle of solid in the capillary introduces errors far larger than the variations in viscosity which the viscometers were designed to measure, it is of the greatest importance to clean the tubes thoroughly after each determination with water containing no solid matter in solution or suspended.

In this research, conductivity water made by distillation in a closed apparatus (Hartley, Campbell, and Poolc, Trans., 1908, 93, 428) was used for washing the tubes. Before use it was carefully examined to see whether it contained any solid matter.

The conductivity of water gives no certain indication of its suitability for this purpose, for the conducting impurities remaining in a sample of good, distilled water are volatile (carbon dioxide and ammonia) and have no effect in the viscometer, whilst, on the other hand, organic impurities or suspended solids render the water useless, although their presence is not indicated by conductivity determinations. Consequently those samples of water which showed no suspended solid were chosen rather than those with a low conductivity. The average conductivity of the water used was

about  $1 \times 10^{-6}$  mho at  $18^\circ$ . The water was quite free from organic impurities.

In spite of all precautions, the tubes frequently became contaminated with dust. When this happened, the tube was charged with a few c.c. of nitric acid and one drop of alcohol, and left overnight.

The presence of dust is betrayed by (1) the irregularity of the results; (2) the failure of the tube to give the same time of flow for water after washing and drying.

After cleaning, the tube is dried by gentle heating, while a current of air, freed from dust by passage through cotton-wool, is drawn through it.

*Filling.*—The viscometers are filled by pipettes of such content as to fill them from the middle of the upper to the middle of the lower bulb. With this arrangement the alteration of hydrostatic pressure due to small variations in the volume filled in by the pipette is a minimum. The liquid (and, if necessary, the pipette) to be used is first brought to the temperature at which the experiment is to take place. The error of the pipettes was measured by weighing successive fillings of water. The greatest variation in six fillings of an 8.7 c.c. pipette was 0.0022 c.c. Since the average diameter of the lower bulbs of the viscometers at their widest parts was 3.8 cm., the greatest error occasioned by variations in the volume of liquid delivered by the pipette will be

$$\frac{0.0022}{1.92 \times \pi} = 0.000194 \text{ cm.}$$

in the head of liquid, and since the average head is 10.6 cm. of water, the error so occasioned is only 0.002 per cent., which is considerably less than the errors in determining the times of flow. The use of a pipette for filling the viscometer is therefore justified.

When filled, the viscometer is fitted with the apparatus shown in Fig. 2 (A), the object of which is to allow the liquid in the viscometer to be forced up the capillary, and to run down without contact with dusty air. The liquid is forced up by pinching the rubber tubing A, and applying pressure by means of a small hand-bellows at B. The air which enters is freed from dust by a tight cotton-wool plug in C.\* When the liquid has risen above the upper mark, the tube A is released, and the air pressure equalises itself on the two sides of the viscometer. During the actual experiment no air from the outside enters. The friction of the air in A was found to be negligible.

As it is of great importance that the viscometer should be fixed

\* When the liquid in the viscometer is hygroscopic, and in all low temperature experiments the air is dried before passing into B.

rigidly and always in exactly the same position, a special holder was designed [Fig. 2 (B)]. The viscometer is fixed by means of the screw *A* with its wider arm resting in two V grooves *B*, *B* and a cross ( $\times$  in Fig. 2) etched on the capillary, resting upon a line scratched on the side-piece *C*. The whole apparatus, which is constructed of stout brass, is now fitted on the brass plate *D*, three steel points *E*, *E*, *E* fitting exactly into three conical holes *F*, *F*, *F*. The points being fitted, the two parts are fixed together rigidly by a nut which is screwed down on the screw *G*, which passes through a hole in the front plate. (The nut must not be screwed down too tightly, or the steel points may be distorted.)

The back plate is firmly attached to a wooden cross-piece supported by two wooden uprights fixed firmly to the bench and supported by stays so as to be very rigid. The wooden parts were made of well-seasoned wood to avoid warping. With this apparatus the viscometer can be brought to exactly the same position for each determination.

*Temperature.*—Experiments were carried out at 25°, 18°, and 0°. For the experiments at 25° and 18° the viscometers were immersed in thermostats holding 30 to 40 litres of water, which was kept in rapid motion by a good stirrer. Constancy of temperature was secured by Lowry spiral regulators, gas heating being used for the 25° bath, electric for the 18° bath. No variation of temperature was ever observed on a thermometer divided into wide twentieths, which could be read to 0.005°. The 0° bath was a well-stirred mixture of crushed ice and water. It usually remained constant to 0.02° during an experiment. The results were calculated to 0° by the use of a temperature correction.

*Method of Experiment.*—The time of flow is found for pure conductivity water, viscometer and pipette are then dried, and the solution to be determined is filled in. The time of flow is then measured several times. Finally, the viscometer and pipette are again cleaned and dried, and the water value is again determined. This precaution is necessary, as the water values sometimes slowly increase during successive fillings, owing to contamination with organic matter or incomplete washings, and the change is so small as to escape notice in any other way. In most of the determinations performed in this research, the original and final water values agreed to 0.2 sec. In a few cases, where it was obvious by the appearance of a large and irregular water value after a constant solution value that contamination had occurred in the final water filling only, the original water value was used in calculation.

*Calculation of Results.*—The simple Poiseuille law gives:

$$\eta/\eta_0 = p^t/p_0^t \eta_0$$

where  $\eta$  = viscosity,  
 $t$  = time of flow,  
 $p$  = hydrostatic pressure in the tube, and  
 $\eta_0$ ,  $t_0$ , and  $p_0$  are the corresponding values for water.

The average pressure producing flow is that of a column of water equal to the mean difference in level diminished by a quantity expressing the buoyancy of the air in which the experiment takes place, and by a quantity depending on the surface effects, proportional to the surface tension. This pressure has been determined in the course of standardising the tubes. It is equal to:

$$H(s_0 - \lambda) - K\gamma_0,$$

where  $H$  = mean difference of level,

$s_0$  = density of water,

$\lambda$  = „ „ air,

$\gamma_0$  = surface tension of water,

and  $K$  = a constant depending on the form of the apparatus.

All the other terms in this expression being known, the constant can be evaluated.

The pressure for the liquid to be determined will be:

$$H(s - \lambda) - K\gamma.$$

The relative viscosity  $\eta/\eta_0$  is therefore given by the expression:

$$\frac{H(s - \lambda) - K\gamma}{H(s_0 - \lambda) - K\gamma_0} \cdot \frac{t}{t_0},$$

or

$$\frac{t}{t_0} \cdot \frac{H(s - \lambda) - K\gamma}{P(s_0 - \lambda)},$$

where  $P$  is the hydrostatic pressure in cm. of water as measured in standardisation:

$$\text{or} \quad \frac{t}{t_0} \cdot \frac{s - \lambda}{s_0 - \lambda} \cdot \frac{H - K\gamma/s}{P},$$

where the small correction  $\lambda$  is omitted from the surface-tension factor.

It is to be noted that no kinetic energy correction is to be applied in calculating the results of experiments with viscometers in which the capillary opens into a reservoir of the same liquid. The correction calculated by earlier observers (Hagenbach, *Pogg. Ann.*, 1860, 109, 385; Finkener, see Gartenmeister, *Zeitsch. physikal. Chem.*, 1891, 6, 524) is only applicable when the liquid flows from the capillary directly into the air. In viscometers of Ostwald type, however, the gain of kinetic energy at the beginning of the capillary is balanced by a loss of kinetic energy on emerging from the capillary into the lower bulb. The net increase of kinetic energy is therefore negligible, especially in viscometers of the slow-flow type described in the foregoing. Grüneisen has shown that

the introduction of such a correction into the  $\eta$  values in standardising a good tube entirely destroys the regularity of the results. I have therefore followed his practice, and omitted any correction for kinetic energy.

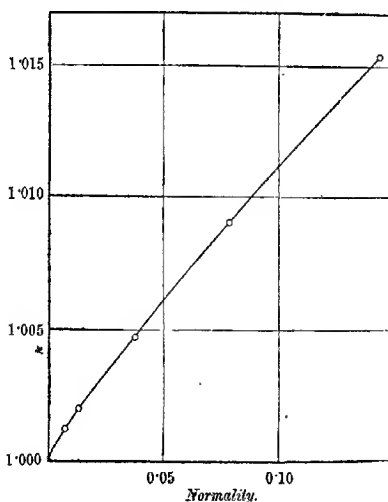
The times of flow for water in the viscometers used are given in the following table:

TABLE III.—*Times of flow for water (in seconds).*

Viscometer.	Time of flow at 25.01°.	Time of flow at 18°.	Time of flow at 0°.
4	1023.8	1207.7	2058.8
E	800.2	943.5	1604.4
S	703.6	830.3	1411.6
A	—	6013.9	—
B	—	7381.1	—

The slow tubes A and B were only used for very dilute solutions. Since the Grüneisen correction for these determinations would have

FIG. 5.



been negligible, these tubes were not standardised. The viscosity determinations are given in tables IV, V, and VI. The viscosities of the solutions at 18° are calculated from the equation developed above.

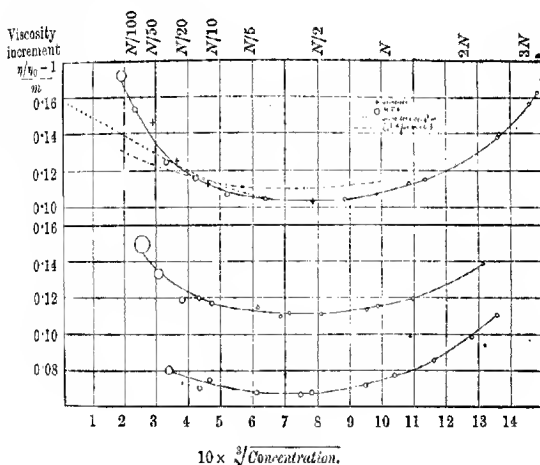
The surface tensions are interpolated from the values of

Gradenwitz (*Diss.* Breslau, 1902) and Piepenstock (*Diss.* Munich, 1908). These determinations were unfortunately only carried out at 18°. The introduction of the surface-tension correction into the results at 25·01° and 0° has therefore been impossible. At these temperatures the relative viscosities are calculated by the simple formula

$$\eta/\eta_0 = \frac{t(s-\lambda)}{t_0(s_0-\lambda)}.$$

For the purpose of comparison, the uncorrected viscosities at 18° are included in table V.

FIG. 6.



The viscosities of the more dilute solutions at 18° are plotted in Fig. 5, while the molecular viscosity increments at the three temperatures are given by Fig. 6. Fig. 6 also contains Grüneisen's values at 18° and the curve given by his equation:

$$\frac{\eta/\eta_0 - 1}{m} = Aa + B(1-a) + Cm.$$

TABLE IV.

Viscosities at 25.01°.

$D_{25}^{25}$ s.	Concentration m.	$10m^{\frac{1}{2}}$	Visco- meter.	Relative viscosity $\eta/\eta_0 = \frac{(s-\lambda)t}{(s_0-\lambda)t_0}$	Mean relative viscosity.	Viscosity increment $\frac{\eta/\eta_0 - 1}{m}$
0.99777 0.99776	0.0174	2.59	S 4	1.00255 1.00265	1.0026	0.149
0.99824 0.99827	0.0290	3.10	S R 4	1.00405 1.00395 1.00395	1.0040	0.133
0.99933 0.99934	0.0567	3.84	R S 4	1.00675 1.0068 1.0066	1.0067	0.119
1.00035 1.00038	0.0825	4.355	S 4 S	1.00935 1.01005 1.0097	1.0099	0.120
1.00135 1.00135	0.1071	4.75	4 S R	1.01265 1.01245 1.01245	1.0125	0.1165
1.00642 1.00642	0.2333	6.155	R S 4	1.0264 1.0266 1.0271	1.0267	0.1145
1.01008 1.01008	0.3238	6.867	4 S	1.0356 1.03525	1.0354	0.1095
1.01159 1.01159	0.3643	7.142	4 S	1.0402 1.0408	1.0405	0.1111
1.01884 1.01882	0.5335	8.136	S R	1.0597 1.0598	1.05975	0.1110
1.03240	0.9668	9.533	4 R	1.0979 1.09805	1.0980	0.1181
1.03656 1.03660	0.9663	9.886	4 S R	1.1117 1.11145 1.1104	1.1112	0.1151
1.05134 1.05146	1.316	10.96	R S	1.1567 1.1567	1.1567	0.1181
1.09364 1.09385	2.2719	13.146	S R	1.31515 1.3151	1.3151	0.1387
1.17009 1.17006	3.8541	15.678	S R	1.74095 1.74055	1.74075	0.1922
1.20848 1.20833	4.578	16.60	4	2.0577	2.0577	0.2310
1.28344 1.28340	5.849	18.02	R 4	3.027 3.024	3.0255	0.346

TABLE V.  
Viscosities at 18°.

Solution made up by weight]	Concentration <i>m</i> .	$10^{10} \eta$ .	$D_{20}^{20} = \alpha$ .	Surface tension (relative to water) $\gamma$ .	Viscometer. Relative viscosity $\frac{\eta}{\eta_0} = \frac{L - \lambda}{L_0 - \lambda} \cdot \frac{H \cdot K \gamma}{P \cdot \frac{1}{\rho}}$	$\frac{H}{P} = 10 \frac{99}{60} k = 0.39$ .	Mean relative viscosity.	Mean relative vis- cosity (uncorr.).	Viscosity increment (uncorr.).
[Solution made up by weight]	0.00724	1.93	0.99892	1.0004	$\frac{A}{B}$	1.00122 1.00127	1.00124	1.00125	0.172
0.99760	0.0131	2.36	0.99916	1.0007	$\frac{A}{B}$	1.00200 1.00190	1.00200	1.00201	0.153
0.99759			0.99915		$\frac{A}{B}$	1.00190			
0.99758	0.0379	3.36	1.00016	1.0014	$\frac{S}{R}$	1.00047 1.00047 1.00047 1.00047	1.0047	1.0047	0.124
0.99858					$\frac{A}{B}$	1.00047			
0.99858					$\frac{A}{B}$	1.00047			
0.99858					$\frac{A}{B}$	1.00047			
1.00019	0.0784	4.28	1.00183	1.0023	$\frac{S}{R}$	1.00095 1.00089	1.00095	1.00090	0.115
1.00022			1.00183		$\frac{R}{K}$	1.00092			
1.00285	0.1446	5.25	1.00452	1.0036	$\frac{S}{R}$	1.0156 1.0153	1.01545	1.01535	0.106
1.00285			1.00453		$\frac{S}{R}$	1.0153			
1.00771	0.2653	6.43	1.00051	1.0061	$\frac{S}{R}$	1.0278 1.0278	1.0278	1.0276	0.104
1.00771			1.00051		$\frac{S}{R}$	1.0278			
1.02563	0.7334	8.89	1.02769	1.0151	$\frac{S}{R}$	1.0737 1.0737	1.0737	1.0731	0.1039
1.02562			1.02768		$\frac{S}{R}$	1.0737			
1.05003	1.283	10.87	1.05245	1.0273	$\frac{S}{R}$	1.1411 1.1411	1.14395	1.1429	0.1113
1.05001			1.05245		$\frac{R}{K}$	1.1411			
1.05811	1.471	11.37	1.06066	1.0313	$\frac{S}{R}$	1.1697 1.17015	1.1699	1.16865	0.1147
1.05806			1.06061		$\frac{R}{K}$	1.1699			
1.10498	2.528	13.62	1.10812	1.0508	$\frac{S}{R}$	1.3497 1.34995	1.34985	1.3172	0.1373
1.10498			1.10812		$\frac{R}{K}$	1.34995			
1.10644	2.550	13.66	1.10959	1.0512	$\frac{S}{R}$	1.3579 1.3579	1.3579	1.3552	0.1393
1.10643			1.10956		$\frac{R}{K}$	1.3579			
1.13341	3.120	14.61	1.13685	1.0618	$\frac{S}{R}$	1.4906 1.4906	1.4906	1.48695	0.1561
1.13342			1.13685		$\frac{R}{K}$	1.4906			
1.13343	3.279	14.66	1.14475	1.0648	$\frac{S}{R}$	1.5366 1.53685	1.5367	1.5327	0.1624
1.14122			1.14475		$\frac{R}{K}$	1.53685			
1.1968	4.363	16.34	1.2008	1.0812	$\frac{S}{R}$	1.9346 1.9346	1.9346	1.9274	0.2125
1.1970			1.2010		$\frac{R}{K}$	1.9346			



TABLE VI.  
Viscosities at 0°.

Dye or [Solution made up by weight]	Concen- tration m.	10m <sub>1</sub>	D <sub>0</sub> <sup>0</sup>	Visco- meter.	Relative viscosity $\eta = \frac{(s-\lambda)\ell}{(s_0-\lambda)\ell_0}$	Mean relative viscosity.	Viscosity incre- ment $\frac{\eta/\eta_0-1}{m}$
				4	1.0032		
				R	1.0032	1.0032	0.080
				S	1.0032		
[Solution made up by weight]	0.0401	3.42	1.00161 1.00161				
1.00039	0.0833	4.37	1.00347	S	1.0058	1.0058	0.070
1.00038			1.00352				
				4	1.0077		
				R	1.00755	1.0076	0.074
				4			
				4	1.0156		
				R	1.0153	1.01545	0.0675
				4			
				4	1.0278		
				S	1.0279	1.0278	0.0665
				4	1.02775		
				R	1.0278		
				4	1.0324		
				R	1.03255	1.0325	0.0675
				4	1.0326		
				4	1.0818		
				S	1.0818	1.0616	0.0718
				R	1.0818		
				4	1.0873		
				S	1.0875	1.0875	0.0772
				4	1.08775		
				4	1.1344		
				R	1.1346	1.1345	0.0865
				S	1.1344		
				4	1.2067		
				R	1.20675	1.2067	0.0984
				S	1.2066		
				4	1.2768		
				R	1.2771	1.2770	0.1104
				S	1.2771		
				4	1.2770		

*Discussion of Results.*—The viscosities determined at 18° agree very satisfactorily with those obtained by Grüneisen. The values obtained for the most dilute solutions, however, differ considerably from those calculated from the formula proposed by him. The course of the curve given by Grüneisen's equation:

$$\frac{\eta/\eta_0-1}{m} = A\alpha + B(1-\alpha) + Cm$$

is shown by the dotted line in Fig. 6. When  $m=0$ , that is, at infinite dilution,  $\alpha=1$  and  $\frac{\eta/\eta_0-1}{m} = A$ . The increment curve ought

therefore to cut the axis of ordinates at a distance  $A$  from the origin. The value of  $A$  given by Grüneisen is 0.15868. The actual course of the increment curve is, however, quite different. The values obtained in the most dilute solutions are already much greater than this value, and the curve is still rising.

It may be noted that the most dilute point obtained by Grüneisen himself also lies considerably higher than the value calculated from his equation. Nor is this an isolated case. Out of ten salts investigated by him at sufficiently great dilution, in eight the most dilute solutions give values too high for his equation. The determination of  $\frac{\eta/\eta_0 - 1}{m}$  for these dilute solutions involves a very large

experimental error, as has been indicated by the size of the circles round the determined points in Fig. 6. The general nature of the phenomenon nevertheless precludes the view that these high values are due to errors of determination, for, if that were the case, the determinations should be equally distributed above and below the calculated curve.

These considerations, together with the determinations at greater dilutions than Grüneisen's, show that, although his equation represents the facts over a certain range, it is not valid for all concentrations.

Grüneisen's equation contains the assumption that the effects of ion and undissociated salt respectively are distinct and separable, and that each is in all cases proportional to the concentration of the component considered. The second assumption can only be true if the process of solution is simply a mechanical mixing.

There is general agreement among physical chemists that the process of ionisation in electrolytes is accompanied by combination between the ions and the water molecules. Since water is a highly associated substance and consists of a mixture of simple and polymerised molecules, the extraction of water molecules from the system by the ions of the salt must be accompanied by a readjustment of the water equilibrium, polymerised molecules breaking down in order to restore the equilibrium. The effect of the ions on the viscosity of the system is therefore twofold: (1) the simple mixture effect, increasing the viscosity by reason of the great size of the hydrated ions; (2) the effect on the water equilibrium.\*

\* It should be noted that the effect of the salt on the water equilibrium does not involve a change in the equilibrium constant, but is simply a dilution effect similar to that observed by Dixon and Peterkin on diluting nitrogen peroxide with an inert gas (Trans., 1899, 75, 613). Thus, if the concentrations of simple and polymerised molecules in pure water be  $c_1$  and  $c_2$ , and the addition of an ionised substance lead to the extraction of  $x$  simple molecules of water, the concentrations of simple and poly-

The disappearance of the maximum density phenomenon when salts are dissolved in water shows that the effect on the water equilibrium is a depolymerisation. This effect will therefore lead to a diminution of viscosity. The diminution will not, however, depend alone on the concentration of the ions, but also on the amount of polymeride present. The effect will thus slowly decrease with successive additions of salt.

Another factor of which we must not lose sight is the change in size of the solvent envelope round the ion, the amount of water combined with each ion becoming greater on dilution.

In the following pages an attempt has been made to deduce a theoretical connexion between the viscosity of a solution and the molecular and ionic phenomena involved in its formation.

It has been tacitly assumed in the above that viscosity is a direct function of molecular size. The general validity of this relation is established by the following facts:

(1) Liquids which are known to be highly associated have usually also a high viscosity. The following examples may be cited:

	Association Factor.*	Viscosity at 20°.†
Propyl alcohol .....	2.25	0.0223
isoPropyl alcohol .....	2.86	0.0243
$\alpha\beta$ -Dihydroxypropane .....	(large)	0.4479
Glycerol .....	(very large)	10.69 (at 18.26°)‡
Ethyl alcohol.....	2.74	0.01202
Acetic acid .....	3.62	0.01222
Ethyl acetate.....	0.99	0.00151
Ethyl ether .....	0.99	0.00237

\* Ramsay and Shields, *Trans.*, 1893, **63**, 1089.

† Gartenmeister, *Zeitsch. physikal. Chem.*, 1891, **6**, 524.

‡ O. G. Jones, *Phil. Mag.*, 1894, [v], **37**, 451.

(2) The work of Heydweiller (*Wied. Ann.*, 1895, **59**, 193) on the viscosity of liquids at high temperatures. The viscosity of water diminishes much more rapidly than that of unassociated liquids when the temperature is raised from 0° to 50°. Above 50°, when the association is small, the rate of diminution is approximately the same as that of unassociated liquids.

merised molecules in the solution will be  $c'_1$  and  $c'_n$ , where (neglecting the change of volume on solution)

$$c_1 + nc_n = c'_1 + nc'_n + x,$$

and

$$\frac{c'_n}{c_n} = \frac{c'_1}{c_1} = k,$$

from which it follows that, since  $x$  is a positive quantity,

$$\frac{c'_n}{c_n} < \frac{c'_1}{c_1}.$$

or that the extraction of simple molecules by the salt leads to a diminution in the association of the water remaining.

(3) The effect of pressure on the viscosity of water (Cohn, *Wied. Ann.*, 1892, **45**, 666). An increase of pressure always brings about an increase in viscosity, in the case of non-associated liquids. At low temperatures the viscosity of water, however, first diminishes with increase of pressure, reaches a minimum value, and then rises in the normal manner. Since the association of water is accompanied by an increase of volume, as is shown by the maximum density phenomenon, the effect of pressure must be to break down the associated molecules. The marked diminution in viscosity, which is superimposed on, and in the initial stages entirely masks, the normal effect of pressure, can only be occasioned by this diminution in molecular size.

(4) The effect of different ions on the viscosity of water is in the reverse order of their mobilities, for example:

Salt.	Viscosity of N/10-solution at 18°.	Mobility of cation.
* Lithium nitrate .....	1.0113	42.6
† Sodium " .....	1.0044	52.6
‡ Potassium " .....	0.9941	75.5
§ Cesium " .....	0.9933	78.8

\* Applebey.

† Grueisen, *loc. cit.*

‡ Unpublished result kindly communicated by Mr. T. R. Merton.

There is much evidence to show that ions of small mobility are heavily loaded with water molecules, and are thus larger than the more mobile ions.

Since the ions in a salt solution are enclosed in a water envelope, it is probably justifiable to neglect the specific chemical difference between hydrated ion and water-molecule, and to assume a rigid connexion between mean molecular volume and viscosity. As the simplest assumption, it has been supposed that these quantities are directly proportional.\*

The different molecular species present in a salt solution are:

- (a) Simple water molecules,  $H_2O$ ;
- (b) associated water molecules, assumed to be triple,  $(H_2O)_3$ ;
- (c) ions, hydrated to an unknown extent,  $Li^+ + xH_2O$ ,  $NO_3^- + yH_2O$ ;
- (d) undissociated molecules, possibly combined with water,  $LiNO_3$ ;
- (e) in strong solutions salt complexes,  $(LiNO_3)_n$ .

The two kinds of water molecule are in kinetic equilibrium with one another. Their proportions in pure water can be obtained from the association constant in the following manner:

\* Dunstan and Thole have shown that these quantities are approximately proportional for different organic liquids which are not associated (*Proc.*, 1907, **23**, 19).

Let  $a$  be the association factor for water at  $18^\circ$ .

$c_1$  " " concentration of single molecules  $H_2O$  in gram-molecules per litre.

$c_3$  " " concentration of triple molecules  $(H_2O)_3$  in gram-molecules per litre.

Then 
$$\frac{3c_3 + c_1}{c_3 + c_1} = a,$$

and  $54c_3 + 18c_1 = 1000s$ , where  $s$  is the density of water.

Then 
$$(3-a)c_3 = (a-1)c_1, \text{ or } c_3 = c_1 \frac{a-1}{3-a},$$

and 
$$\frac{54(a-1)}{3-a}c_1 + 18c_1 = 1000s,$$

whence 
$$c_1 = \frac{1000s(3-a)}{36a} \text{ and } c_3 = \frac{1000s(a-1)}{36a}.$$

Now for the equilibrium  $(H_2O)_3 \rightleftharpoons 3H_2O$

we have

$$\frac{c_3}{c_1^3} = k,$$

whence

$$k = \frac{1296(a-1)a^2}{10^6 s^2 (3-a)^3}.$$

Taking at  $18^\circ$  Ramsay's value of 1.65 for the association constant (*Zeitsch. physikal. Chem.*, 1895, 15, 106) and 0.99863 as the density,  $k = 0.0009347$ .

The value of  $k$  thus found can be used to calculate the effect of the salt on the water equilibrium.

Taking a solution of weight normality  $m$ , density  $s$ , and degree of ionisation  $\alpha$ ,

1000 c.c. of the solution weigh  $1000s$  grams.

Of this the salt accounts for  $Mms$  grams (where  $M$  = molecular weight of the salt), leaving  $(1000 - Mms)$  grams of water.

Now, if  $w$  be the average hydration number for the two ions, that is, if 1 gram-molecule of the salt, completely ionised, combines with  $2w$  molecules of water, the amount of water thus removed from the system is:

$$2masw \times 18 \text{ grams.}$$

The free water is therefore reduced to:

$$(1000 - Mm - 36masw)s \text{ grams.}$$

Letting  $c_1$  and  $c_3$  as before represent the concentration of single and triple molecules, we have:

$$54c_3 + 18c_1 = (1000 - Mm - 36masw)s,$$

or, since  $c_3 = k \times c_1^3$ ,

$$54kc_1^3 + 18c_1 = (1000 - Mm - 36masw)s,$$

from which  $c_1$  and  $c_3$  can be obtained (most conveniently by trial).  
The total number of gram-molecules in a litre of solution is:

$$c_1 + c_3 + ms(1 + a).$$

The mean molecular volume is therefore:

$$\frac{1000}{c_1 + c_3 + ms(1 + a)}.$$

The mean molecular volume in pure water is:

$$\frac{1000}{c'_1 + c'_3},$$

where  $c'_1$  and  $c'_3$  are the concentrations of single and triple molecules in pure water.

On the assumption that viscosity is proportional to mean molecular volume, we have therefore:

$$\frac{\eta}{\eta_0} = \frac{c'_1 + c'_3}{c_1 + c_3 + ms(1 + a)}.$$

Owing to the absence of accurate determinations of several of the quantities involved in this treatment, and especially of the hydration numbers at different concentrations, it is at present impossible to submit the equation to a quantitative test. It may, however, be noted that the course of the calculated viscosity increment curve corresponding with the equation agrees with the actual form observed in one important respect. The calculated curve shows the phenomenon of a minimum increment at about 0.5 normal, as does the observed curve. As an illustration of this there has been included in Fig. 6 a curve representing the viscosity increment calculated on the assumption that the hydration of the ions is constant and equal to 6.3 molecules of water per ion. The curve has been calculated with Ramsay's value for the association of water at 18°, and with values of  $a$  obtained from Kohlrausch and Maltby's conductivity determinations (*Sitzungsber. K. Akad. Wiss. Berlin*, 1899, 655) by means of the relation:

$$a = \frac{\lambda}{\lambda_\infty} \times \frac{\eta}{\eta_0},$$

where  $\lambda$  = molecular conductivity, and  $\lambda_\infty$  = molecular conductivity at infinite dilution.

The calculated curve differs considerably from the observed, although they are of the same general shape. A very inconsiderable change in hydration is, however, sufficient to bring the curves into harmony. The values of the hydration necessary have been found by trial, and are collected in the following table:

Normality.	Hydration calculated from viscosity in gram-molecules of water per gram-molecule of ion.
0.00724	8.0
0.0131	7.5
0.0379	6.5
0.0784	6.3
0.1446	6.1
0.2653	6.1
0.7034	6.05
1.0	6.05

These values are in good agreement with those obtained by other methods for various salts. For lithium nitrate itself Wympere (*Proc. Roy. Soc.*, 1907, **79**, 576) obtained a value of 13 for the hydration of a molecule of the salt in a normal solution (from the "neutral salt effect" in the inversion of sucrose). For potassium chloride in normal solution, Philip (*Trans. Faraday Soc.*, 1907, **3**, 145) gives 9.4, and Caldwell (*Proc. Roy. Soc.*, 1906, **78**, 290) 11 molecules of water per molecule of salt, whilst for more dilute solutions Bousfield (*Proc. Roy. Soc.*, 1904, **76**, 563) gives 12. In accordance with its smaller mobility, the lithium ion seems to be rather more hydrated than the potassium ion.

From the results obtained at 25.01°, the same method of calculation gives values for the hydration numbers about 0.3 higher than those obtained at 18°. A similar small increase of hydration with temperature is indicated by the conductivity values of many salts (Noyes, see Washburn, *Tech. Quart.*, 1908, **21**, 425).

For other salts, Grüneisen's values at 18° give:

Salt.	Normality.	Hydration in mols. per ion.
Sodium nitrate .....	0.1	3.4
	0.05	3.5
Lithium chloride .....	0.1	8.8

Salts which are less hydrated than these, however, give impossible values. Thus, potassium nitrate gives small, and caesium nitrate larger, negative values. In view of these negative values, it may be recalled that Rennie, Higgin and Cooke (*Trans.*, 1908, **93**, 1162) found that caesium nitrate diminished the rate of solution of copper in nitric acid, whilst sodium nitrate and lithium nitrate greatly accelerated the action.

To sum up, this method of calculating the hydration, like the methods depending on the concentrating effect of neutral salts in chemical reactions, gives values approximating to the truth for substances which are much hydrated, but gives values too low for less hydrated substances. It is not improbable that the failure of all these methods of calculation in this respect depends on some hitherto unconsidered factor in the equilibrium of salt solutions.

which becomes of increasing importance as the hydration diminishes.

*Summary.*—1. It has been found possible to construct viscometers in which the flow of liquid is so slow that, for solutions whose viscosity differs little from that of water, Poiseuille's law is obeyed with an error of not more than one part in 10,000. The methods used in testing the viscometers are described.

2. A correction has been introduced for the variation in surface effects when different liquids are used in the viscometer.

3. Determinations of density and viscosity have been carried out with lithium nitrate solutions at 0°, 18°, and 25° over a large range of concentration.

4. The formula of Grüneisen is found not to represent the phenomena of dilute solution.

5. A method of calculating the viscosity of salt solutions from their hydration numbers, or vice versa, has been described. The application of this method to the viscosities of lithium nitrate solutions at 18° gives results consistent with the estimates of ionic hydration made by other observers.

6. The application of the method to other salts is discussed.

I am greatly indebted to Mr. D. H. Nagel and Mr. H. B. Hartley for much valuable advice and encouragement during the progress of this work.

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## Organic Chemistry.

**Theory of the Formation of Ethylene.** ROBERT KREMANN (*Monatsh.*, 1910, 31, 211-220).—Experiments have been made on the reaction between ethylene and sulphuric acid by heating the two together in the proportions 1:4 grammols. The experiments were conducted in a sealed bulb attached to a manometer, and the mercury adjusted so that the volume was kept constant. At all temperatures up to  $110^{\circ}$ , slow absorption took place until equilibrium had been established (at  $57^{\circ}$   $p=115$ , at  $99^{\circ}$   $p=240$ , and at  $167^{\circ}$   $p=270$  mm.). Above  $111^{\circ}$  absorption took place for a short time, but was followed by a rapid increase of pressure due to secondary reactions, for example, the formation of carbon monoxide and sulphur dioxide. Even at the higher temperatures, it was found possible to minimise the effects of the secondary reactions by allowing the mixture to remain at a lower temperature until a pressure was obtained which was close to that corresponding with the higher temperature, and then to plunge the vessel into the bath at the higher temperature. If the pressure was correct, no diminution occurred, but after some time there was a rapid increase of pressure due to the secondary reactions. The value of  $Q$  (the algebraic sum of the heat of formation of 1 gram-mol. of ethyl hydrogen sulphate from the alcohol and acid and the heat of solution of this sulphate in the liquid phase) has been calculated from the equation  $\log p_1/T_1 - \log p_2/T_2 = Q/R \cdot T_2 - T_1/T_1 T_2$ , and has a value of about  $-3.4$  Cal.

Similar experiments have been made by heating ethyl hydrogen sulphate (1 mol.) with sulphuric acid (3. mols.), but experimental difficulties were experienced owing to the secondary reactions. At  $99^{\circ}$  the pressure rose rapidly at the beginning, then more slowly, remained constant for a short time, and again increased, probably owing to the secondary reactions which are facilitated by the catalytic influence of the carbon formed during the reaction.

The results agree with the view that alcohol and sulphuric acid react instantaneously, forming water and ethyl hydrogen sulphate, and that the latter then decomposes into ethylene and sulphuric acid.

J. J. S.

**Preparation of Organic Iodides from the Corresponding Bromides and Chlorides.** HANS FINKELSTEIN (*Ber.*, 1910, 43, 1528-1532. Compare Perkin and Duppa, *Annalen*, 1859, 112, 185; von Romburgh, *Abstr.*, 1883, 303).—One of the best methods of replacing the chlorine or bromine of an organic compound by iodine is to treat with an acetone solution of sodium iodide. In many cases the reaction is instantaneous, and in all cases where reaction proceeds, a precipitate of sodium chloride or bromide is formed.

The relative reactivities of halogen derivatives towards sodium iodide do not appear to be the same as their reactivities towards

water or methyl alcohol; thus, primary alkyl bromides react most readily with sodium iodide, and the tertiary least readily.

The method does not work with acyl chlorides or with chloro- or bromo-compounds, which yield unstable iodo-derivatives. This is usually the case with compounds containing several carbonyl, carboxyl, or phenyl groups; in such cases one of the following changes occurs: (1) Formation of an ethylene linking, for example,  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid yields cinnamic acid; (2) ring formation, for example, tetrabromo-*o*-xylene,  $\text{C}_6\text{H}_4(\text{CHBr}_2)_2$ , yields the compound  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CHBr} \\ \diagup \quad \diagdown \\ \text{CHBr} \end{smallmatrix}$ ; (3) union of two molecules, for example, ethyl bromo-

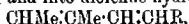
malonate yields ethyl ethanetetra-carboxylate. Ethyl dibromomalonate yields ethyl ethylenetetra-carboxylate. Benzophenone chloride yields dichlorotetraphenylethane, and benzophenone bromide yields tetraphenylethylene.

The following iodo-compounds have been prepared:

Amyl iodide, isopropyl iodide, trimethylene iodide, ethyl iodoacetate, *p*-nitrobenzyl iodide, *o*-, *m*-, and *p*-xylylene iodides. J. J. S.

Constitution of the Alcohols arising from the Condensation of Secondary Alcohols with their Sodium Derivatives. MAKINO, GUERRET (*Compt. rend.*, 1910, 150, 979—981. Compare Abstr., 1901, i, 307; this vol., i, 149).—The constitution of certain alcohols described in previous communications has been established by a study of their oxidation products. Dioctyl alcohol is shown to be  $\eta$ -methyl-pentadecan-*o*-ol.  $\eta$ -Methylpentadecan-*o*-one has b. p. 172—174°/21 mm.,  $D_{20}^0$  0.846, and forms a semicarbazone, m. p. 195—197° (corr.). Trisec-butyl alcohol is  $\gamma$ -methyl- $\epsilon$ -ethylnonan- $\eta$ -ol. W. O. W.

Action of Organo-magnesium Compounds on Tiglic Aldehyde and the Optical Behaviour of the Products. PAUL ABELMANN (*Ber.*, 1910, 43, 1574—1588).—A number of unsaturated alcohols have been prepared by dropping tiglic aldehyde into an ethereal solution of magnesium ethyl bromide or the corresponding ethyl, propyl, isopropyl, isobutyl, or isoamyl bromides, and hydrolysing the resulting products. The yields vary from 40 to 70%. These alcohols can be transformed into the corresponding chlorides by boiling with concentrated hydrochloric acid according to Norris's method (*Austr.*, 1907, i, 1034), and into diolefine hydrocarbons,



by heating with potassium hydrogen sulphate or acetic anhydride and sodium acetate. The same hydrocarbons are formed by the action of quinoline on the chlorides, or by boiling the alcohols with hydrobromic acid? All the hydrocarbons are characterised by a high exaltation in their molecular refractions.

$\gamma$ -Methyl- $\Delta^2$ -pentene-3-ol,  $\text{CHMe}:\text{CMe}:\text{CHMe}:\text{OH}$ , has b. p. 55—56°/20 mm. or 84—86°/88 mm., or at 139—141°/760 mm. (slight decomp.). It has  $D_{20}^0$  0.8793 and  $n_D^{20}$  1.4428. The acetate has b. p. 153—155°, and the chloride,  $\text{C}_6\text{H}_5\text{Cl}$ , b. p. 41—43°/34 mm.  $\gamma$ -Methylpentane- $\beta\gamma\delta$ -triol,  $\text{OH}:\text{CHMe}:\text{CMe}(\text{OH}):\text{CHMe}:\text{OH}$ , obtained

by oxidising the alcohol with dilute permanganate, has b. p. 133—135°/13 mm. or 159—160°/41 mm., and solidifies when kept. The triacetyl derivative,  $C_{13}H_{20}O_6$ , has m. p. 123° and b. p. 143—146°/16 mm.

$\gamma$ -Methyl- $\Delta^2$ -hexene- $\delta$ -ol,  $CHMe:CMc:CHEt:OH$ , has b. p. 71—73°/28 mm., 94—95°/80 mm., or 154—155°/760 mm.,  $D_4^{20}$  0.8857 and  $n_D^{20}$  1.44914. The acetate has b. p. 167—170°, and the chloride,  $C_8H_{15}Cl$ , b. p. 51°/11.5 mm.

$\gamma$ -Methylhexane- $\beta\gamma\delta$ -triol,  $OH\cdot CHMe:CMc(OH)\cdot CHEt:OH$ , has b. p. 163°/36 mm., and yields a triacetate,  $C_{13}H_{22}O_6$ , b. p. 146—147°/12 mm.

$\gamma$ -Methyl- $\Delta^2$ -heptene- $\delta$ -ol,  $CHMe:CMc:CHPr:OH$ , has b. p. 74—77°/17 mm.,  $D_4^{20}$  0.8814, and  $n_D^{20}$  1.45614. The acetyl derivative,  $C_{10}H_{17}O_2$ , has b. p. 79—83°/16 mm., and the chloride,  $C_8H_{15}Cl$ , b. p. 53—54°/11 mm.

$\gamma$ -Dimethyl- $\Delta^2$ -hexene- $\delta$ -ol,  $CHMe:CMc:CH(OH)\cdot CHMe_2$ , has b. p. 66—71°/14 mm. or 86—88°/42 mm.,  $D_4^{20}$  0.8727, and  $n_D^{20}$  1.45214. The acetate,  $C_{10}H_{18}O_2$ , has b. p. 103—106°/57 mm., and the chloride,  $C_8H_{15}Cl$ , b. p. 58—60°/21 mm.

$\gamma$ -Dimethyl- $\Delta^2$ -heptene- $\delta$ -ol,  $CHMe:CMc:CH(OH)\cdot CH_2\cdot CHMe_2$ , has b. p. 113—114°/70 mm.,  $D_4^{20}$  0.8753, and  $n_D^{20}$  1.45337. The acetate,  $C_{11}H_{20}O_2$ , has b. p. 92—95°/18 mm., and the chloride,  $C_9H_{17}Cl$ , b. p. 55—53°/9 mm.

$\gamma$ -Dimethyl- $\Delta^1$ -octene- $\delta$ -ol,  $CHMe:CMc:CH(OH)\cdot CH_2\cdot CH_2\cdot CHMe_2$ , has b. p. 113—114°/30 mm.,  $D_4^{20}$  0.8762, and  $n_D^{20}$  1.45460. The acetate,  $C_{11}H_{22}O_2$ , has b. p. 159—163°/80 mm., and the chloride,  $C_{10}H_{19}Cl$ , b. p. 83—84°/12 mm.

$\gamma$ -Methyl- $\Delta^{2,3}$ -pentadiene,  $CHMe:CMc:CH:CH_2$ , has b. p. 76—79°,  $D_4^{20}$  0.7576, and  $n_D^{20}$  1.45427.

$\alpha\beta\gamma$ -Tetrabromo- $\gamma$ -methylpentane,  $CHBrMe:CBBrMe:CHBr:CH_2Br$ , is an unstable liquid, as is also the dihydrobromide,  $C_6H_{12}Br_2$ .

$\gamma$ -Methyl- $\Delta^{2,3}$ -hexadiene,  $CHMe:CMc:CH:CHMe$ , has b. p. 107—108°,  $D_4^{20}$  0.7753,  $n_D^{20}$  1.45146;  $\gamma$ -methyl- $\Delta^{2,3}$ -heptadiene,

$CHMe:CMc:CH:CHEt$ ,

has b. p. 132—135°,  $D_4^{20}$  0.7783, and  $n_D^{20}$  1.46493. The dihydrobromide,  $C_8H_{16}Br_2$ , has b. p. 109—110°/16 mm.

$\gamma$ -Dimethyl- $\Delta^{2,3}$ -hexadiene,  $CHMe:CMc:CH:CMc$ , has b. p. 114—115°,  $D_4^{20}$  0.7714, and  $n_D^{20}$  1.45457; the dihydrobromide,  $C_8H_{16}Br_2$ , has b. p. 99—103°/16 mm.

$\gamma$ -Dimethyl- $\Delta^{2,3}$ -heptadiene,  $CHMe:CMc:CH:CH\cdot CHMe_2$ , has b. p. 144—146°,  $D_4^{20}$  0.7853, and  $n_D^{20}$  1.46335. The dihydrobromide,  $C_9H_{18}Br_2$ , has b. p. 129—130°/20 mm.

$\gamma$ -Dimethyl- $\Delta^{2,3}$ -octadiene,  $CHMe:CMc:CH:CH\cdot CH_2\cdot CHMe_2$ , has b. p. 164—167°,  $D_4^{20}$  0.7939, and  $n_D^{20}$  1.46650. The dihydrobromide,  $C_{10}H_{20}Br_2$ , has b. p. 136—139°/18 mm.

J. J. S.

Modification of Couturier and Meunier's Process for the Preparation of Pinacone. A. H. RICHARD and PAUL LANGLAIS (*Bull. Soc. chim.*, 1910, [iv], 7, 454—458).—The process depends on the action of acetone on magnesium amalgam, the compound  $Mg \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix} \begin{smallmatrix} CMc_2 \\ CMc_2 \end{smallmatrix}$  being first formed, and yielding pinacone hydrate on addition of water (Abstr., 1902, i, 335; 1905, i, 326).

The modification consists in using commercial acetone instead of the pure ketone, and in employing acetone to wash out the pinacone in place of boiling water. It is unnecessary to maintain an atmosphere of dry carbon dioxide in the flask if the process is carried out rapidly. The yield of pinacone varies from 60 to 70% of the theoretical. The other products formed are *isopropyl alcohol*, *mesityl oxide*, *isophorone*, a viscous *dihydric alcohol*,  $C_8H_{14}O_2$ , b. p. 100–108°/17 mm. or 196°/760 mm., and a *trihydric alcohol* (*β-cyclo-trimethylhexan-β-γ-triol*),  $OH \cdot CMe_2 \cdot CMe(OH) \cdot CH_2 \cdot CMe_2 \cdot OH$ , b. p. 150–155°/20 mm., which has been synthesised by Bouveault and Levallois by the action of magnesium methyl iodide on methyl citramalate.

The exact working conditions and particulars of the isolation of these products are given in the original.  
T. A. II.

**Oxidation of Δγ-Acetylenic Glycols. Synthesis of α-Hydroxy-acids.** GEORGES DUPONT (*Compt. rend.*, 1910, 150, 1523–1525. Compare this vol., i, 85).—Oxidation of Δγ-acetylenic glycols of the type  $HO \cdot CRR' \cdot C \equiv C \cdot CRR' \cdot OH$  by means of potassium permanganate results in the formation of α-hydroxy-acids; the yields, however, are not good, since further oxidation takes place, resulting, with tertiary glycols, in the production of oxalic acid and a ketone.

β-Dimethyl-Δγ-hexinen-βε-diol yields α-hydroxyisobutyric acid, whilst ββε-tetraphenyl-Δγ-butinen-βε-diol,  $OH \cdot CPh_2 \cdot C \equiv C \cdot CPh_2 \cdot OH$ , m. p. 149–150°, obtained by the action of benzophenone on magnesium acetylene dibromide, gives diphenylglycollic acid with oxalic acid and benzophenone.

The yields are improved by employing the diacetates of the glycols.  
W. O. W.

**Alkaline Hydrolysis of Glyceryl Trinitrate.** ERNST BERL and MAX DELPY (*Ber.*, 1910, 43, 1421–1429).—The authors have hydrolysed an alcoholic solution of glyceryl trinitrate at 4° with alcoholic potassium hydroxide, and from the products have obtained ammonia, potassium nitrite and nitrate, carbon dioxide, hydrogen cyanide, oxalic acid, mesoxalic acid, α-glyceryl dinitrate, and unchanged glyceryl trinitrate.  
C. S.

**General Method for the Direct Preparation of Thiols from Alcohols by Catalysis.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, 150, 1217–1221. Compare this vol., i, 294).—When the vapour of an alcohol mixed with hydrogen sulphide is passed over heated thorium oxide, a thiol is produced; the reaction is represented as: (1)  $ThO_2 + 2C_nH_{2n+1} \cdot OH = ThO(OC_nH_{2n+1})_2 + H_2O$ ; (2)  $ThO(OC_nH_{2n+1})_2 + 2H_2S = ThO_2 + 2C_nH_{2n+1} \cdot HS + H_2O$ . A sulphide is formed in small quantity and with greater difficulty:  $ThO(OC_nH_{2n+1})_2 + 2C_nH_{2n+1} \cdot HS = ThO_2 + 2(C_nH_{2n+1})_2S + H_2O$ . The thorium oxide acts as a catalyst, and the action is continuous. The hydrogen sulphide employed need not be free from hydrogen.

An excellent yield of the corresponding thiols has been obtained from methyl, ethyl, propyl, isobutyl, isoamyl, and allyl alcohols, keeping the catalyst at 300–360°. Benzyl alcohol gave a good yield of

thiol, accompanied by the normal sulphide and some stilbene. In the case of secondary alcohols, the yields are less satisfactory; the following compounds have been prepared: propan- $\beta$ -thiol; cyclohexanethiol, b. p. 155° (compare Mailhe and Murat, this vol., i, 374); 2-methylcyclohexanethiol, b. p. 161°; 3-methylcyclohexanethiol, b. p. 168°; 4-methylcyclohexanethiol, b. p. 169°.

Thiophenols may be prepared by this method at 430–480°, but in no case does the yield exceed 17%. At 450°, phenol gives a small amount of diphenyl ether.

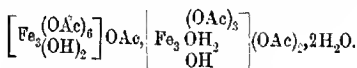
W. O. W.

**Formation of Acetic and Formic Acids by the Hydrolysis of Substances Containing Lignin.** WILLIAM E. CROSS (*Ber.*, 1910, 43, 1526–1528).—Acetic and formic acids are produced when substances rich in lignin are hydrolysed with 1% sulphuric acid at 130°, or even 110°.

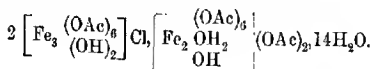
The substances used were straw, jute, and various woods. Cellulose does not yield volatile acids, and pentosans but very little, so that the acids come from the lignin. It would thus appear that lignin contains acetyl and formyl groups, in addition to methoxy-groups.

With pine wood, the ratio acetic : formic acid is 4 : 1. J. J. S.

**Simple Preparation of a Crystalline Ferric Acetate.** RUDOLF F. WEINLAND and ERNST GUSSMANN (*Zeitsch. anorg. Chem.*, 1910, 87, 250–252).—When concentrated solutions of ferric chloride (1 mol.) and sodium acetate (3 mols.) are mixed and allowed to evaporate slowly, large, dark red prisms of ferric acetate are obtained. The addition of sodium platinichloride produces a characteristic precipitate of hexa-acetotriferric platinichloride (this vol., i, 296). The red salt is a compound of the mono- and di-acetate of this base:



Lithium chloride forms with this solution a salt:



C. H. D.

**Mixed Compounds of Salts and Anhydrides of Fatty Acids.** DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1910, [iv], 7, 461–464).—Frauzen has shown (*Abstr.*, 1908, i, 937) that compounds, analogous to Gerhardt's compound of potassium acetate and acetic anhydride, may be obtained with other acetates, and that for sodium and potassium two series of such products exist, represented by the formulæ:  $\text{Ac}_2\text{O} \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{M}'$  and  $\text{Ac}_2\text{O} \cdot \text{CH}_3 \cdot \text{CO}_2\text{M}'$ . It is now shown that compounds analogous with those represented by the second formula may be obtained with acetic anhydride and the salts of the homologues of acetic acid, but that compounds represented by the first formula are not obtainable in these cases. The substances obtained crystallise

well, possess rhombic symmetry, and show marked double refraction. On exposure to the air, the crystals are transformed in a few minutes into microscopic cubes, and, when warmed at  $80^{\circ}$ , become isotropic without losing their form. The isotropic crystals melt at  $150^{\circ}$ ; on further heating, the liquor effervesces and then passes into anisotropic crystals, which finally change at a higher temperature into amorphous solids. The original compounds probably have the general formula  $\text{Ac}_2\text{O}(\text{CO}\cdot\text{R})\text{M}'$ , and the first change from anisotropic to isotropic crystals probably accompanies a change represented by the equation:  $\text{R}\cdot\text{CO}_2\text{M}'(\text{CH}_3\text{CO})_2\text{O} \rightarrow (\text{R}\cdot\text{CO}_2\text{M}')_2(\text{CH}_3\text{CO})_2\text{O}$ . The substances are obtained by boiling the appropriate salt with acetic anhydride during twenty minutes, filtering, and cooling, when colourless needles of the desired products are deposited. Compounds with the following salts are described.

*Sodium formate*.—This softens and becomes opaque at  $82^{\circ}$ , begins to clear at  $114^{\circ}$ , melts at  $154^{\circ}$ , effervesces at  $174^{\circ}$ , and re-solidifies at  $185^{\circ}$ .

*Sodium propionate*.—This softens at  $80^{\circ}$ , melts at  $154^{\circ}$ , effervesces at  $174^{\circ}$ , and re-solidifies at  $185^{\circ}$ . *Sodium butyrate*.—This melts at  $155^{\circ}$ , effervesces at  $180^{\circ}$ , and re-solidifies at  $188-190^{\circ}$ .

*Sodium valerate*.—This, on heating, undergoes the series of changes mentioned under sodium formate at the following corresponding temperatures  $82^{\circ}$ ,  $154^{\circ}$ ,  $175^{\circ}$ ,  $180^{\circ}$ . Exposed to the air this compound forms a mixture of isotropic cubes, crystalline substances, and isotropic droplets; the last of these eventually form monoclinic crystals showing extinction at about  $45^{\circ}$ , and analogous to sodium acetate crystals.

T. A. H.

**Preparation of Pivalic Acid.** A. H. RICHARD and P. LANGLIS (*Bull. Soc. chim.*, 1910, [iv], 7, 464-468).—Tiemann and Semmler have shown (*Abstr.*, 1898, i, 629) that methyl ketones on oxidation by sodium hypochromite furnish bromoform and acids containing one carbon atom less than the parent ketones, and Denigès has confirmed this behaviour for pinacolin (*Abstr.*, 1903, i, 606). This process has now been applied to pinacolin for the preparation of pivalic acid, of which a yield equal to 70% of the theoretical was obtained. Full details of the method of preparation are given in the original. The by-products are unchanged pinacolin, bromoform, carbon tetrabromide, tribromopinacolin, and trimethyl-lactic acid. The last-mentioned substance probably originates through the formation of some dibromopinacolin, which by the action of alkali would pass into trimethyl-pyruvic acid, and this, by the further action of alkali, would furnish trimethyl-lactic acid (compare Wittorff, *Abstr.*, 1900, i, 422), and a trial with dibromopinacolin under the conditions prescribed confirmed this view. Boeseken has described already this method of preparing pivalic acid, but his observation that isobutyric acid is a by-product could not be confirmed.

T. A. H.

**Some Salts of Gallipharic Acid, a Fatty Acid obtained by the Oxidation of cycloGallipharic Acid.** HERMANN KUNZ-KRAUS and PAUL MANICKE (*Arch. Pharm.*, 1910, 248, 294-302).—At examination of the following salts of gallipharic acid confirms the

supposition previously advanced (Abstr., 1904, i, 587), that this acid is a pentadecanecarboxylic acid,  $C_{15}H_{31}CO_2H$ . Sodium salt,  $C_{15}H_{31}O_2Na$ ; potassium salt; potassium hydrogen salt,  $C_{15}H_{31}O_2K$ ,  $C_{15}H_{31}O_2K$ , m. p. 103°; calcium and barium salts; calcium hydrogen salt,  $(C_{15}H_{31}O_2)_2Ca$ ,  $2C_{15}H_{31}O_2$ , m. p. 87°; barium hydrogen salt,  $(C_{15}H_{31}O_2)_2Ba$ ,  $2C_{15}H_{31}O_2$ , m. p. 98°; cadmium salt, m. p. 125—140°; cadmium hydrogen salt,  $(C_{15}H_{31}O_2)_2Cd$ ,  $2C_{15}H_{31}O_2$ , m. p. 98.5°; silver salt; silver hydrogen salt,  $2C_{15}H_{31}O_2Ag$ ,  $C_{15}H_{31}O_2$ ; copper salt; copper hydrogen salt,  $(C_{15}H_{31}O_2)_2Cu$ ,  $C_{15}H_{31}O_2$ , m. p. 98°; ferric salt, m. p. 78°; basic lead salt,  $10(C_{15}H_{31}O_2)_2Pb$ ,  $Pb(OH)_2$ .

C. S.

**Isomerisation of Oleic Acid by Displacement of the Double Linking.** ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1910, 150, 1525—1528).—The reaction of Saytzeff (Abstr., 1887, 386), in which oleic acid is treated with hydrogen iodide and the product boiled with alcoholic potassium hydroxide, gives rise to a mixture containing at least four acids. In addition to regenerated oleic acid there is formed hydroxystearic acid, m. p. 83—84°,  $\Delta^2$ -elaidic acid, and  $\Delta^2$ -elaidic acid. The separation of these acids is described, and Saytzeff's isooleic acid shown to be a mixture.

$\Delta^2$ -Elaidic acid has also been obtained by partial hydrogenation of the corresponding stearic acid by the method described previously (this vol., i, 356). The compound occurs in tablets, m. p. 53°, and yields a dihydroxystearic acid, crystallising in elongated laminae, m. p. 98.5°.

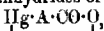
W. O. W.

**Two New Isomerides of Stearic Acid.** ALBERT ARNAUD and SWIGEL POSTERNAK (*Compt. rend.*, 1910, 150, 1245—1247. Compare Abstr., 1909, i, 630; this vol., i, 356).—When fused stearic acid is saturated with hydrogen iodide an oily mixture containing two isomeric diiodostearic acids is produced. On hydrolysis this yields the original stearic acid, together with two new isomerides crystallising in pearly lamellae, and a moniodo-acid, which resists further hydrolysis.  $\Delta^2$ -Stearic acid, m. p. 47.5°, yields suberic acid on oxidation, and unites with iodine, forming  $\theta$ -di-iodoelaidic acid, needles, m. p. 67°.  $\Delta^2$ -Stearic acid, m. p. 47°, yields sebacic acid on oxidation, and furnishes  $\omega$ -di-iodoelaidic acid, lamellae, m. p. 45°;  $\kappa$ -ketostearic acid crystallises in rhombic lamellae, m. p. 73.5°.

The iodoelaidic acids, m. p. 23—24° and 39°, described in a previous paper are now shown to be  $\theta$ -iodo- $\Delta^2$ -elaidic acid and iodo- $\Delta^2$ -elaidic acid respectively.

W. O. W.

**Preparation of Aqueous Soluble Compounds from the Anhydrides of Hydroxymercurycarboxylic Acids.** WALTER SCHÖELLER and WALTHER SCHRAUTH (D.R.-P. 221483).—When the hydroxymercurycarboxylic anhydrides of the general formula



where A is an aliphatic or aromatic residue, are slowly added to an aqueous solution containing molecular equivalents of alkali sulphite,





by heating a solution of mercuric gluconate (Abstr., 1908, i, 123) has been applied to mercuric *L*-arabonate, whereby a poor yield of *L*-erythrose has been obtained.

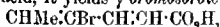
A freshly prepared solution of arabinolactone has  $[\alpha]_D$  about  $70^\circ$ , and one of arabonic acid has  $[\alpha]_D -10^\circ$ ; both solutions in course of time attain to the same value,  $[\alpha]_D -51.5^\circ$ . This behaviour, which is also exhibited by gluconic acid, galactonic acid, rhammonic acid, and their lactones, appears to be a characteristic property of acids of the sugar group, and can be utilised for their identification.

Methyl arabinonate, obtained by keeping a solution of arabinolactone in somewhat diluted methyl alcohol over lime or by heating calcium arabinonate, methyl alcohol, and sulphuric acid on the water-bath, exhibits an initial rotation,  $[\alpha]_D -6.7^\circ$ , which changes to  $-42.7^\circ$  by keeping, the change being due to the gradual decomposition of the ester into the acid and methyl alcohol. C. S.

**Formation of Lævulic Acid from Hexoses.** WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 387—390).—There are two stages in the formation of lævulic acid from hexoses: hydroxymethylfurfuraldehyde is first formed by elimination of water, and is subsequently transformed into lævulic acid and formic acid. Ihl and Pechmann's test for hexoses is explained by the fact that warming hydroxymethylfurfuraldehyde with diphenylamine yields a substance of dark blue colour. A. J. W.

**Action of the Electric Discharge on Acetaldehyde in Presence of Hydrogen.** ADOLPHE BESSON and A. FOURNIER (*Compt. rend.*, 1910, 150, 1238—1241. Compare Losanitsch, this vol., i, 1).—When the vapour of acetaldehyde mixed with a small amount of hydrogen is submitted to the action of the silent electric discharge, a brilliant phosphorescence is produced, and a liquid formed having an odour of pickled herrings. This has been found to contain acetic acid and homologous acids, acetone, diethyl ketone, diacetyl, unidentified viscous substances, and an acid,  $C_4H_6O_3$ , having the properties of  $\beta$ -hydroxybutyric acid. W. O. W.

**$\alpha$ -Bromocrotonaldehyde.** P. L. VIGUIER (*Compt. rend.*, 1910, 150, 1431—1433. Compare Abstr., 1909, i, 691).—The constitution of  $\alpha$ -bromocrotonaldehyde has been proved by its oxidation to  $\alpha$ -bromocrotonic acid. A more rapid method for preparing the substance than that previously described consists in brominating crotonaldehyde and adding the product to a 50% solution of sodium acetate at  $150$ — $170^\circ$ . The aldehyde is separated by distillation in steam. When heated with pyridine and malonic acid, it yields  $\gamma$ -bromosorbic acid,



m. p.  $133^\circ$ ; the potassium salt forms pearly lamellæ (compare Riedel and Straube, Abstr., 1909, i, 550). The cyanohydrin decomposes when distilled in a vacuum; on hydrolysis, it yields  $\beta$ -bromo- $\alpha$ -hydroxy- $\Delta^2$ -pentenoic acid,  $CHMe.CBr.CH(OH).CO_2H$ , m. p.  $123$ — $124^\circ$ ; the potassium salt crystallises in prisms, the silver salt in long, brilliant needles. W. O. W.

**Production of Aldehyde Resins by the Carbonisation of Wood in Closed Vessels.** RENE P. DUCHEMIN (*Bull. Soc. chim.*, 1910, [iv], 7, 473—479).—A résumé is first given of the work of Kleeberg (*Abstr.*, 1891, 1199), Trillat (*Annales*, 1891, 263, 312), Blumer (*Fr. Pat.* 329982 of 1903), Delaire (*Fr. Pat.* 361509 of 1905), Baekeland (*Mon. Sci.*, 1909, 421) and others on the condensation of formaldehyde with phenols in the presence of alkalis or acids to form resinous products, which in some cases resemble copal or lac.

In connexion with the investigation of a new process of manufacturing crude acetates (*Fr. Pat.* 375314 and 402907 of 1903), the author has observed the formation of similar resins in passing the acid vapours from the distillation of wood, first through an apparatus for the removal of tar, and then into scrubbers containing alkaline liquids. The latter are at first brown or black, but become golden-yellow as the passage of the vapours continues, and finally deposit black, plastic masses, which after heating at 200° become hard and possess a conchoidal fracture. Similar products are obtained by (1) heating crude pyroligneous acid under a reflux condenser, (2) condensing "heavy oils" recovered from crude pyroligneous acid with formaldehyde in presence of hydrochloric acid, (3) heating the mother liquors recovered from the manufacture of crude acetates, and then adding water. These products have m. p. 60—70°, dissolve in alkaline solutions, and are re-precipitated by acids. They are soluble in acetone, wood-spirit, or methyl acetate, but the extent of their solubility depends on the temperature to which they have been heated. These resins probably result from the interaction of aldehydic with phenolic substances, both these groups of products occurring in the vapours from the distillation of wood. It is suggested that wood tar may consist of a solution of these resins in phenols (compare Lingner, *Fr. Pat.* 328971 of 1903).

The resins obtained in distilling wood-spirit over alkalis differ from the foregoing in their lighter colour and in being insoluble in alkalis.

T. A. H.

**Preparation of Pinacolin.** A. H. RICHARD and P. LANGLIS (*Bull. Soc. chim.*, 1910, [iv], 7, 459—461).—The preparation was effected (1) by heating pinacone hydrate with a 30% solution of sulphuric acid during three hours at 150° and steam-distilling the mixture, or (2) by heating pinacone hydrate with dry oxalic acid in a calcium chloride bath. The first process gave a 90%, and the second a 75% yield of crude pinacolin. The oxalic acid was used several times, but eventually became coated with tarry matters and had to be replaced by fresh material.

On fractionation, the crude pinacolin yielded, as more volatile by-products, acetone and diisopropenyl (Couturier, *Abstr.*, 1893, i, 244; Kondakoff, *Abstr.*, 1901, i, 62), and, as less volatile by-products, unaltered pinacone, mesityl oxide, and isophorone. The diisopropenyl probably resulted from complete dehydration of pinacone, but the mesityl oxide and isophorone were probably present as impurities in the pinacone hydrate used (see this vol., i, 455), and the acetone and a

small quantity of mesitylene found probably resulted from the action of acids on these impurities. T. A. H.

**Reduction of Aliphatic Diketones.** EDMOND E. BLAISE and A. KÖHLER (*Bull. Soc. chim.*, 1910, [iv], 7, 416—420).—In a previous paper (Abstr., 1909, i, 204) it has been shown that aliphatic diketones can be synthesised by the action of the chlorides of dihasic acids on mixed organic compounds of zinc. Perkin has observed (Trans., 1891, 59, 214) that nonane- $\beta\beta$ -dione on reduction with sodium yielded a cyclic pinacone, and it was therefore of interest to ascertain within what limits the formation of a ring depends on the relative positions of the two carbonyl groups. Reduction of octane- $\beta\eta$ -dione, decane- $\gamma\delta$ -dione, and undecane- $\gamma$ -dione furnished no cyclic pinacones, but only the corresponding glycols, and, similarly, attempts to dehydrate undecane- $\gamma$ -diol were unsuccessful.

Octane- $\beta\eta$ -dione, on reduction by Perkin's method (*loc. cit.*), yielded the secondary cyclic alcohol already described by Perkin (Trans., 1890, 57, 245), and octane- $\beta\eta$ -diol, b. p. 138—139°/15 mm., a viscous liquid with a sweetish acid taste, and readily soluble in organic solvents; its diphenylurethane, m. p. 126°, crystallises in long needles from a mixture of light petroleum and ether.

Decane- $\gamma\delta$ -dione under similar conditions yielded a hydrocarbon, b. p. 70—72°/1 mm., and the corresponding glycol, m. p. 72°, which crystallises in silky needles from a mixture of ether and light petroleum. The diphenylurethane, m. p. 137°, crystallises from ether in needles, and is greasy to the touch. Undecano- $\gamma$ -dione furnished a trace of pinacone (?), b. p. 156°/18 mm., and the corresponding glycol, m. p. 80·5°, crystallising from warm ether in long, silky needles. The diphenylurethane, m. p. 84—85° (approx.), crystallises from a mixture of benzene and light petroleum in splendid needles. T. A. H.

**New Synthesis of Natural and Racemic Erythritol.** H. PARSSELLE (*Compt. rend.*, 1910, 150, 1343—1346. Compare Abstr., 1909, i, 691; Lespieau, Abstr., 1907, i, 173).— $\Delta^2$ -Butylene- $\gamma\delta$ -oxide,  $\text{CH}_2$

$\text{O} \rightarrow \text{CH} \cdot \text{CH} \cdot \text{CH}_2$ , prepared by heating  $\delta$ -bromo- $\Delta^2$ -butylene oxide with potassium hydroxide, is a very mobile liquid, b. p. 70°/760 mm.,  $D_4^{20}$  0·9006,  $D_4^{20}$  0·87,  $n_D^{20}$  1·416. When shaken with water and a few drops of sulphuric acid, a solid polymeride is formed, and the solution, on distillation in a vacuum, yields erythrol ( $\Delta^2$ -butylene- $\gamma\delta$ -diol),  $\text{OH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CH}_2$ , as a syrupy liquid, b. p. 91—93°/12 mm.,  $D_4^{14}$  1·05,  $n_D^{14}$  1·469; the diphenylurethane has m. p. 125—126°. When the diol is treated with barium permanganate, a syrup is obtained, which deposits natural erythritol when sown with a crystal of this substance. The residual liquid contains racemic erythritol, isolated and identified by conversion into the dibenzoylacetel. W. O. W.

**Aloinose, the Sugar from Aloin.** EUGÈNE LEGER (*Compt. rend.*, 1910, 150, 983—986; *Bull. Soc. chim.*, 1910, [iv], 7, 479—485. Compare Abstr., 1903, i, 356; 1904, i, 907).—Further experimental

details are given for the preparation of aloinose from barbaloin. The sugar has  $[\alpha]_D$  57.3° to 58.5°, and forms an *osazone*, crystallising in elongated, pointed lamellæ. On hydrolysis with alcoholic sulphuric acid, nataloin yields small quantities of a non-crystalline, levorotatory sugar closely resembling Paloinose. W. O. W.

**Nitration of Cotton Wool. Cellulose.** PRIEST (*Zeitsch. angew. Chem.*, 1910, 23, 1009—1018).—A résumé of previous work on cellulose and its nitrates is given. The action of various alkalis on gun-cottons prepared in different ways has been investigated.

Gun-cotton prepared from cotton wool treated in the usual manner gave a residue of 8% when left in contact with 0.5*N*-sodium hydroxide solution during ten days, whereas a gun-cotton prepared from a strongly bleached cotton wool left a residue of only 1.7% insoluble matter, after similar treatment during four days. Gun-cotton prepared from mercerised cotton gave a residue of 13% after ten days. Similar experiments with a concentrated ammonium sulphide solution gave a residue of 49.5% after eight days using ordinary gun-cotton, a residue of 37.5% with gun-cotton from strongly bleached cotton, and 52% with a gun-cotton from mercerised cotton. Treatment of a gun-cotton with alkalis affords a method for determining the manner in which the cotton had been treated before nitration.

The resistance of various gun-cottons towards alkalis is in the order of the resistance of the materials from which they were obtained.

The action of alkalis on collodion wools prepared from samples of cotton wool which have been subjected to different treatment has also been examined, and the results obtained are similar to those with gun-cottons. When concentrated ammonium sulphide is used, complete hydrolysis is brought about in four days, since the residue left contains no nitrogen.

During nitration, especially when the amount of water present is large, hydroxycelluloses are formed, and the final products are mixtures of esters of cellulose and hydroxycelluloses.

Treatment of the esters with ammonium sulphide appears to bring about a partial conversion of cellulose into hydroxycelluloses.

J. J. S.

**Mercury Fulminate.** ANDREAS SOLONINA (*Zeitsch. Schieß Sprengstoffwesen*, 1910, 5, 41—46, 67—72).—A discussion of the various methods usually employed for the preparation of mercury fulminate, with particulars of numerous experiments by the author, and microphotographs showing the crystalline structure of the products.

The second paper contains details of experiments for the purification of mercury fulminate for analysis; the employment of ammonia is not considered satisfactory, but the preparation of the crystalline compound with pyridine, its subsequent decomposition with water, and the final estimation of mercury by electrolysis is recommended.

F. M. G. M.

**Calcium Cyanamide and some Compounds Prepared from it.**  
 FR. REIS (*Biochem. Zeitsch.*, 1910, 25, 460--476).—Cyanamide in a state of purity is best prepared from calcium cyanamide by precipitation with the theoretical quantity of oxalic acid calculated from the calcium content of the calcium cyanamide. An alkaline solution of calcium cyanamide rapidly decomposes at the ordinary temperature, and still more rapidly on heating, dicyanodiamide in varying amounts being formed; an acid solution is, at the ordinary temperature, stable.

Warm permanganate solution has practically no action; Devarda's alloy reduces the cyanamide rapidly to ammonia, and gives a large increase in the quantity of dicyanodiamide formed. The optimum conditions for the conversion into dicyanodiamide are obtained by the use of carbonates of the alkalis and alkaline earths at 65°. The decomposition undergone in the presence of soil may be due to bacterial action, if the concentration be not so great as to inhibit the action of the organisms. The presence of ferric oxide has the catalytic effect of accelerating the decomposition of cyanamide into carbamide. No compound of cyanamide and iron could be formed. G. S. W.

**Cryohydrates of Ammonium and Potassium Thiocyanates.**  
 ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 423--427).

—The author has investigated the cryohydrates of these salts by Flawitzky's method of cooling mixtures. Ammonium thiocyanate forms the cryohydrate,  $\text{NH}_4\text{CNS} \cdot 5 \cdot 851\text{H}_2\text{O}$ , at  $-25 \cdot 2^\circ$ , and the potassium salt,  $\text{KCNS} \cdot 5 \cdot 349\text{H}_2\text{O}$ , at  $-31 \cdot 2^\circ$ ; these compositions are in accord with Guthrie's law (this Journ., 1875, 530), the smaller proportion of water present in the cryohydrate corresponding with the lower temperature. The lower water-content of the cryohydrate of the potassium salt is also in agreement with the greater solubility of this salt. In the formation of these cryohydrates, the mixtures of salt and snow do not solidify, and the residues left in the refrigerator always consist solely of the excess of salt which has not taken part in the reaction, so that it is highly probable that the action occurs between the snow and anhydrous salt without formation of hydrates.

The m. p.'s of these thiocyanates were given by Pohl (1851) as  $161 \cdot 2^\circ$  for the potassium salt and  $159^\circ$  for the ammonium salt, the latter figure being confirmed by Reynolds (this Journ., 1869, 1). The author obtains the m. p.  $174 \cdot 2^\circ$  for the potassium salt, and  $149 \cdot 5^\circ$  for the ammonium salt, but in the latter case decomposition occurs to some extent. Using these numbers, Flawitzky's law (Abstr., 1906, ii, 153) gives (1) for the ammonium salt, the relation between the polymerisations of the salt and water represented by  $(\text{H}_2\text{O})_x : (\text{NH}_4\text{CNS})_y$ , and the composition of the cryohydrate,  $\text{NH}_4\text{CNS} \cdot 5 \cdot 931\text{H}_2\text{O}$ ; and (2) for the potassium salt, the ratio  $(\text{H}_2\text{O})_x : (\text{KCNS})_y$ , and the composition  $\text{KCNS} \cdot 5 \cdot 332\text{H}_2\text{O}$  for the cryohydrate. If potassium and ammonium thiocyanates form a eutectic mixture, the constituents should be present in the proportion of 3 mols. to 2 mols. T. H. P.

**Diastatic Scission of Lactose Derivatives.** H. BERRY and ALBERT RANG (*Compt. rend.*, 1910, 150, 1366—1368. Compare Abstr., 1908, i, 1031).—Lactoseaminoguanidine nitrate (Wolf, Abstr.,

1896, i, 78) has  $[\alpha]_D^{20}$  8.4°, and m. p. 225—227° on the Maquenne block. The digestive juice of snails hydrolyses this substance with formation of galactose and dextroseaminoguanidine. The same ferment decomposes lactosemicarbazone into galactose and dextrosesemicarbazone, a similar fission occurring in the case of Schoorl's lactosecarbamide (*Rec. trav. chim.*, 1903, 22, 31).

The experiments support Fischer's view that lactose is the galactoside of dextrose.

W. O. W.

**Instability of Alloxan.** ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1910, 32, 809).—A sample of alloxan, which had been kept for several years in a bottle, suddenly underwent spontaneous decomposition and caused a violent explosion. This behaviour does not appear to have been noticed previously.

MANSTON T. BOGERT (*ibid.*, 809—810) records a similar explosion in a case containing alloxan amongst other fine organic chemicals.

F. G.

**Formation of Hydrogen Cyanide.** ARMAND JORISSEN (*Bull. Acad. roy. Belg.*, 1910, 224—233).—The first part of the paper deals with the conclusions arrived at by the author and others concerning the production of hydrogen cyanide in plants (compare Jorissen, *Abstr.*, 1885, 181; Jorissen and Hairs, *Abstr.*, 1892, 502; Hébert, *Abstr.*, 1899, ii, 377; Greshoff, *Abstr.*, 1907, ii, 121; and Treub, *Ann. Jar. bot. Buitenzorg*, 1905, [ii], 4, 86).

Although Seyewetz and Poizat have recently shown (*Abstr.*, 1909, i, 146) that a large number of aromatic compounds give hydrogen cyanide when boiled with a mixture of nitric and nitrous acids, this observation cannot be used in support of the hypothesis that the naturally occurring hydrogen cyanide is formed by the action of nitrates on organic substances, since the conditions are entirely different. The author, however, finds that a number of substances when acted on with dilute nitric acid at the ordinary temperature in the light, form appreciable quantities of hydrogen cyanide; thus when 0.5 to 1.0 gram of morphine, brucine, vanillin, quinal, catechol, resorcinol, sucrose, lactose, or honey is kept in contact with 100 c.c. of a 3.4% aqueous solution of nitric acid at the ordinary temperature and exposed to light, a small amount of hydrogen cyanide is formed. The reaction, like that described by Seyewetz and Poizat, is inhibited by carbamide, but is unaffected by asparagine. Addition of potassium nitrite solution to the nitric acid immediately after the addition of vanillin does not cause the instantaneous formation of hydrogen cyanide.

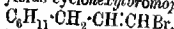
E. H.

**Application of Magnesium in Organic Chemistry.** VICTOR GRIGNARD (*Chem. Zeit.*, 1910, 34, 529; *Bull. Soc. chim.*, 1910, [iv], 7, 453—454).—In reply to Barbier (this vol., i, 308), the author mentions that he has in common with others, who have written on the application of magnesium in organic chemistry, referred to the importance in this connexion of Barbier's synthesis of dimethylheptenol by the use of magnesium methyl iodide. He adds, however,

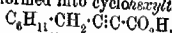
that Barbier's method is a modification of the Saytzeff reaction, in which two substances merely react in presence of magnesium, whilst his own method is derived from the work of Frankland, Wanklyn, and Wagner on mixed organo-magnesium compounds and their application.

T. A. H.

*cycloHexylallylene* [*cycloHexylpropylene*] and *cycloHexylpropinene*. B. DE RESSÉGUIER (*Bull. Soc. chim.*, 1910, [iv], 7, 431-434).—*cycloHexylpropylene*,  $C_6H_{11} \cdot CH_2 \cdot CH : CH_2$ ,  $D_4^{20}$  0.8196,  $n_D^{20}$  1.45362, b. p. 148—149°, prepared by the action of allyl bromide on magnesium *cyclohexyl* bromide (compare Tiffeneau, Abstr., 1904, i, 872), is a colourless liquid of pleasant odour (compare Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1905, 37, 630). The *dibromide* has  $D_4^{20}$  1.537 and b. p. 143—144°/16 mm. On treatment with potassium hydroxide in alcohol, it yields *cyclohexylbromopropylene*,



$D_4^{20}$  1.2063, h. p. 122—124°/17 mm., a colourless liquid, and finally *cyclohexylpropinene*, b. p. 165—170°. The latter was not purified, but was converted into the sodium derivative, and the latter by the action of carbon dioxide transformed into *cyclohexyltetraic acid*,



m. p. 74—75°, which crystallises from carbon tetrachloride. The *methyl ester* has b. p. 135°/15 mm.,  $D_4^{20}$  1.010,  $D_4^{25}$  0.9978,  $n_D^{25}$  1.48354, corresponding with mol. ref. 51.41 in place of the calculated value 50.43 (compare Moureu, Abstr., 1906, ii, 1).

T. A. H.

**Freezing of Mixtures of Isomeric Benzene Derivatives.** GIUSEPPE BRUNI (*Zeitsch. Elektrochem.*, 1910, 16, 285).—The phenomena described by Fischer (this vol., i, 309) are quite in accordance with the regularities observed by the author. In general, position isomerides in the benzene series do not form solid solutions, but substances having analogous substituting groups in the same position do.

T. E.

**Derivatives of Ethylbenzene and of *iso*Propylbenzene.** EALING SCHREINER (*J. pr. Chem.*, 1910, [ii], 81, 557—564).—*p*-Chloro-ethylbenzene is readily obtained by heating ethyl bromide and chlorobenzene with aluminium chloride on the water-bath. An individual product is not obtained when bromobenzene is used. *o*- and *p*-Nitro-ethylbenzene are easily obtained by dissolving ethylbenzene in fuming nitric acid and fractionating the product under diminished pressure. By reduction with tin and hydrochloric acid, each yields the corresponding amino-derivative, from which by diazotisation and treatment with potassium iodide, *o*-iodoethylbenzene, b. p. 226°,  $D_4^{20}$  1.6189,  $n_D^{20}$  1.59408, and *p*-iodoethylbenzene, m. p. -11°, b. p. 230°,  $D_4^{20}$  1.6095,  $n_D^{20}$  1.59094, are obtained. The *iododichloride*,  $C_6H_4Et \cdot ICl_2$ , of the former, obtained by the direct action of chlorine at 0°, is an unstable, yellow, crystalline substance decomposing at 63°; treatment with sodium hydroxide yields, not the iodoso-compound, but the *iodonium hydroxide*,  $(C_6H_4Et)_2 \cdot OH$ , since the addition of potassium iodide to the solution yields the *iodide*,  $(C_6H_4Et)_2 I_2$ , which decomposes at 126°.



*p*-Iodoisopropylbenzene, which can be prepared by heating isopropylbenzene, iodine, and iodic acid in slightly diluted acetic acid for six hours, forms a *iododichloride*,  $C_9H_7Pr^i \cdot ICl_2$ , a citron-yellow powder decomposing at  $110^\circ$ , from which the *iodoso*-compound,  $C_9H_7Pr^i \cdot IO$ , decomposing at  $165^\circ$  (the *acetate*,  $C_9H_7Pr^i \cdot I(OAc)_2$ , has m. p.  $83^\circ$ ), the *iodoxy*-compound, exploding at  $191^\circ$ , and the *iodonium iodide*, decomposing at  $140^\circ$ , are readily obtained. C. S.

**Phenylsulphoxyacetic Acid.** II. RUDOLF FUMMERER (*Ber.*, 1910, 43, 1401—1412. Compare Abstr., 1909, i, 580).—Phenylsulphoxyacetic acid is obtained by passing dry nitrous fumes into dry ethereal phenylthiolacetic acid; by the addition of petroleum, a brown oil separates, which evolves nitric oxide (?), and yields phenylsulphoxyacetic acid. *Phenylbenzylsulphoxide*,  $CH_2Ph \cdot SOPh$ , m. p.  $125.5^\circ$ , obtained in a similar manner from phenyl benzyl sulphide, does not yield thiophenol by heating with 50% sulphuric acid, and forms benzyl chloride and a little benzaldehyde with alcoholic hydrogen chloride. The preceding sulphoxides are also very conveniently prepared by the oxidation of phenylthiolacetic acid and phenyl benzyl sulphide by 33% hydrogen peroxide in glacial acetic acid. Diethyl sulphide is converted by this oxidising agent, with careful cooling, into diethyl sulphoxide, which forms with a solution of hydroferrocyanic acid, a stable, crystalline *hydroferrocyanide*,  $C_4H_9OS, H_4Fe(CN)_6, H_2O$ , which turns blue at  $140^\circ$ .

Phenylthiolacetic acid is converted by alcoholic hydrogen chloride into the *ethyl ester*, h. p.  $144-145^\circ/14$  mm., an ethereal solution of which yields with sodium a yellowish-white, powdery sodio-derivative, which reacts with ethereal methyl iodide to form *ethyl  $\alpha$ -phenylthiopropionate*,  $SPh \cdot CHMe \cdot CO_2Et$ , b. p.  $139.5^\circ/14.5-15$  mm., an ethereal solution of which also reacts with sodium.

$\alpha$ -Phenylthiopropionic acid, obtained from  $\alpha$ -bromopropionic acid and thiophenol in alkaline solution, is converted by cold hydrogen peroxide in glacial acetic acid into  *$\alpha$ -phenylsulphoxypropionic acid*,  $Ph \cdot SO \cdot CHMe \cdot CO_2H$ , m. p.  $135^\circ$ , which is converted into thiophenol and pyruvic acid by boiling 25% sulphuric acid. The oxidation of ethyl phenylthiolacetate by 33% hydrogen peroxide and glacial acetic acid at  $40-50^\circ$  leads to the formation of *ethyl phenylsulphoxyacetate*, b. p.  $152-154^\circ/3$  mm., a colourless, almost odourless, mobile liquid, which decomposes at  $220-230^\circ$ , yielding thiophenol and ethyl phenylthiolacetate and other products, is decomposed by cold fuming hydrochloric acid with the formation of thiophenol, and is easily hydrolysed by alcoholic potassium hydroxide, which, even when boiling, does not cause the generation of thiophenol.

A migration of oxygen from sulphur to carbon occurs when ethyl phenylsulphoxyacetate is heated with acetic anhydride, whereby *ethyl  $\alpha$ -acetoxypenylthiolacetate*,  $SPh \cdot CH(OAc) \cdot CO_2Et$ , b. p.  $172.5^\circ/15$  mm., is formed. *Phenylthiomethyl acetate*,  $SPh \cdot CH_2 \cdot O \cdot COMe$ , b. p.  $249^\circ/713$  mm., is obtained by heating phenylsulphoxyacetic acid with acetic anhydride, or, better, by the action of lead peroxide on phenylthiolacetic acid in boiling glacial acetic acid; it yields thiophenol very readily by treatment with alcoholic potassium hydroxide. C. S.

Distyrene. CARL LIEBERMANN (*Ber.*, 1900, 43, 1543—1544).—The author agrees, with Erlenmeyer (this vol., i, 309) that the compound described previously (*Abstr.*, 1889, 1196) as distyrene is stilbene. J. J. S.

Triarylmethyls. IV. WILHELM SCHLENK, ANNA HERZENSTEIN, and TORIAS WEICKEL (*Ber.*, 1910, 43, 1753—1758. Compare *Abstr.*, 1902, i, 791; this vol., i, 236, 237).—Gomberg and Cone (*Abstr.*, 1906, i, 414, 821) by the action of silver on  $\omega$ -chlorophenyldiphenylene-methane in presence of air obtained phenyldiphenylenemethyl peroxide; in the absence of air a hydrocarbon was formed, which they could not isolate. When  $\omega$ -chlorophenyldiphenylenemethane is heated in benzene with copper bronze or copper powder in an atmosphere of carbon dioxide, diphenylbis(diphenylene)-ethane,  $\text{C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2$ , is formed. This crystallises in long, obliquely-cut plates, m. p. 205—230° (decomp.), or when heated in sealed tubes in an atmosphere of carbon dioxide, m. p. 254°.

Solutions in organic solvents become more or less brown in colour on heating, the colour vanishing again on cooling. This change is attributed to dissociation into the methyl compound,  $\text{CPh} \cdot \text{C}(\text{C}_6\text{H}_5)_2$ ; it is specially marked in anisole. The colourless solutions do not decolorise iodine solutions; the hot brown solutions rapidly decompose iodine solutions. Bis(diphenyl)bis(diphenylene)-ethane (*loc. cit.*, 238) hardly shows any tendency to dissociate.

Phenyldis(diphenyl)methyl,  $\text{CPh}(\text{C}_6\text{H}_5)_2$ , is now obtained as a colourless powder. This is only slowly soluble in benzene; the solution is at first colourless and then red. Molecular-weight determinations indicate that 80% of the compound is present as methyl derivative. E. F. A.

$\omega$ -Dichlorotetraphenylethane. HANS FINKELSTEIN (*Ber.*, 1910, 43, 1533—1535. Compare Schmidlin and von Escher, this vol., i, 369).— $\omega$ -Dichlorotetraphenylethane can be prepared by the action of sodium iodide on an acetone solution of  $\omega$ -dichlorodiphenylmethane. If a large excess of the iodide is used, tetraphenylethylene is formed, but with a mixture of two parts of the chloro-derivative, 1.4 of sodium iodide, and 10 of acetone, a 75% yield of the dichlorotetraphenylethane can be obtained by keeping at the ordinary temperature for two days. The same product is formed by the addition of chlorine to tetraphenylethylene, although the unsaturated hydrocarbon does not combine with bromine. When heated alone or with indifferent solvents of high boiling point, hydrogen chloride is formed, together with impure tetraphenylethylene. The unsaturated hydrocarbon contains chlorine attached to one of the benzene nuclei.

When the dichloro-derivative is boiled with methyl alcohol, the chief product is  $\beta$ -benzopinacoline. J. J. S.

Preparation of Acylaminophenylsulphonamic Acids. HUGO FEIL and KARL WEISSE (D.R.-P. 221301).—Acylaminophenyl  
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sulphonamic acids and their homologues are readily prepared by heating acylnitroanilines with an aqueous solution of sodium hydrogen sulphite. By the action of halogens in aqueous alkaline solution on these compounds, substituted halogen derivatives are formed; from these the acyl and sulpo-groups are removed by heating with mineral acid and subsequent boiling with alkali hydroxide, yielding halogenated diamines.

If boiled with alkali, the acyl group only is removed, and on acidification the crystalline *anilinesulphonamic acid* is precipitated; this is readily diazotised, yielding *diazobenzenesulphonamic acid*, which by contact with dilute mineral acid is converted into *diazop-aminobenzene*.  
F. M. G. M.

**Trinitro-*p*-anisidine.** FRÉDÉRIC REVERDIN [with A. DE LUC] (*Arch. Sci. phys. nat.*, 1910, [iv], 29, 476—483; *Compt. rend.*, 1910, 150, 1433—1435\*).—When benzoyl-2:3-dinitro-*p*-anisidine (Abstr., 1909, i, 377) is nitrated with nitric acid (D 1.52), first at 5—10°, and then at 60° for five minutes, *nitrobenzoyl-2:3:6-trinitro-*p*-anisidine* is obtained as a felted mass of colourless, slender needles, m. p. 247°. When treated with three times its weight of strong sulphuric acid on the water-bath, it gives on cooling a brilliant red precipitate of the corresponding 2:3:6-trinitro-*p*-anisidine, m. p. 127—128°. From aqueous solutions large, reddish, orthorhombic crystals are obtained [*a:b:c* = 0.738287:1.0812027]. The action of acetic anhydride in the presence of a small quantity of concentrated sulphuric acid gives the *acetyl* derivative,  $C_{19}H_{15}O_6N_6$ ; white needles, m. p. 242°.

One of the nitro-groups (it is not certain which) in trinitro-*p*-anisidine is very reactive. When heated with excess of various bases, compounds of the general formula  $OMe \cdot C_6H(NO_2)_2R \cdot NH_2$  are produced, R representing the residue of the base employed. The *aniline* derivative,  $C_{13}H_{12}O_5N_4$ , has m. p. 148°, and forms brown spangles; the *p*-toluidine derivative,  $C_{14}H_{14}O_5N_4$ , forms brown, prismatic crystals, m. p. 139°; the *monomethylamine* derivative,  $C_8H_{10}O_5N_4$ , crystallises in reddish-violet needles, m. p. 193—200°.

When trinitro-*p*-anisidine is heated in alcoholic solution with sodium acetate, a reddish-brown precipitate of the sodium salt of a *dinitrohydroxy-*p*-anisidine*,  $OMe \cdot C_6H(NO_2)_2(OH) \cdot NH_2$ , is obtained. On the addition of acid to the aqueous solution of this salt, brown needles of the dinitrohydroxy-*p*-anisidine are obtained, m. p. 161°. The *acetyl* derivative is obtained by treatment with acetic anhydride and concentrated sulphuric acid; small, white needles, m. p. 193—194°.

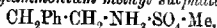
In the nitration of benzoyl-2:3-dinitro-*p*-anisidine another product is formed besides nitrobenzoyl-2:3:6-trinitro-*p*-anisidine. It forms pale yellow needles, and has m. p. 259°. Analysis points to the formula  $C_{14}H_{10}O_6N_4$ , and it is either a benzoyltrinitroanisidine or a nitrobenzoyldinitroanisidine.  
T. S. P.

**Amines. III. Alkylations with Dimethyl Sulphate.**  
**Synthesis of Dimethylphenylethylamine.** TREAT B. JOHNSON and HERBERT H. GUEST (*J. Amer. Chem. Soc.*, 1910, 32, 761—770).—It has been shown previously (Abstr., 1909, i, 785) that methyl iodide reacts with phenylethylamine to form the hydriodide of the original base

\* and *Ber.*, 1910, 43, 1819—1853.

and phenylethyltrimethylammonium iodide, but that the mono- and di-methyl derivatives are not produced. It has now been found that phenylethyldimethylamine,  $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}_2$ , can be prepared by the action of methyl sulphate on phenylethylamine in presence of sodium methoxide. This amine has been obtained in small quantity by Barger (Trans., 1909, 95, 2195) by heating phenylethyl chloride with dimethylamine. When *p*-nitrophenylethylamine (Johnson and Guest, this vol., i, 311) is treated with methyl sulphate, alkylation does not take place, but the amine remains unchanged. Attempts have also been made to prepare secondary and tertiary amines from *p*-nitrophenylethylamine by alkylation with methyl iodide, but without success.

When methyl sulphate is heated with an ethereal solution of phenylethylamine, *phenylethylammonium methyl sulphate*,



m. p. 75—77°, is obtained in the form of lustrous plates, together with a hygroscopic quaternary salt, m. p. 100—110° (decomp.).

Phenylethyldimethylamine, h. p. 200—205°, is a strong base, and absorbs carbon dioxide from the air. The *platinichloride* decomposes at 221°; the *hydrochloride* has m. p. 205°.

When phenylethylmethylamine (Johnson and Guest, *loc. cit.*) is heated with thioacetic acid, *acetyl-p-nitrophenylethylmethylamine*,  $\text{CH}_3\text{Ph}\cdot\text{CH}_2\cdot\text{NMeAc}$ , is obtained as a dark-coloured oil, and, on nitration, yields the *p-nitro-derivative*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMeAc}$ , m. p. 100—101°, which, on oxidation with potassium dichromate, furnishes *p-nitrobenzoic acid*. When *acetyl-p-nitrophenylethylmethylamine* is digested with hydrobromic acid, it is converted into *p-nitrophenylethylmethylamine hydrobromide*; the base was obtained as a heavy, yellow oil. By the action of phenylthiocarbimide on *p-nitrophenylethylmethylamine*,  $\alpha$ -phenyl- $\beta$ -*p-nitrophenylethyl*- $\beta$ -methylthiocarbimide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CS}\cdot\text{NHPh}$ , m. p. 137—138°, is produced, which crystallises in plates.

By reducing *p-nitrophenylethylamine* with tin and hydrochloric acid, *p-aminophenylethylamine* (Johnson and Guest, *loc. cit.*) is produced. When *p-nitrophenylethylamine* is heated with methyl iodide, the hydriodide of the amine is obtained, together with *p-nitrophenylethyltrimethylammonium iodide*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , m. p. 200—201°, which forms hexagonal prisms. E. G.

**Solubility Equilibrium between Phenanthrene and 2:4-Dinitrophenol.** ROBERT KREMAN and F. HOFMEIER (*Monatsh.*, 1910, 31, 201—202).—Phenanthrene forms additive compounds with trinitrobenzene and trinitrotoluene, but not with the dinitro-compounds (Abstr., 1905, i, 77; 1909, i, 29).

An examination of the freezing-point curve of mixtures of phenanthrene and 2:4-dinitrophenol proves that these compounds do not form a definite compound; the curve has only one eutectic point, namely, at 61°.

J. J. S.

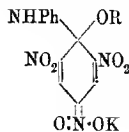
**Picric Acid.** A. STEPANOFF (*Annalen*, 1910, 373, 219—226).—The solubility of picric acid in water is decreased at first by the addition of hydrogen chloride, but reaches a minimum when the solution contains roughly 0.5 millimol. of picric acid and 150 millimol.

of hydrogen chloride in 100 c.c. of the solution, after which the solubility increases as the concentration of hydrogen chloride becomes greater. It seems probable, therefore, that picric acid and hydrogen chloride combine, forming an unstable additive product having the annexed formula, the proportion of which capable of existing in solution will depend on the concentration of the hydrogen chloride. If the quantity of hydrogen chloride is insufficient, the additive compound will decompose, yielding the true trinitrophenol rather than the *aci*-form, since not only do quinonoid compounds tend to pass into benzenoid compounds, but the true trinitrophenol is less soluble than the coloured *aci*-form.

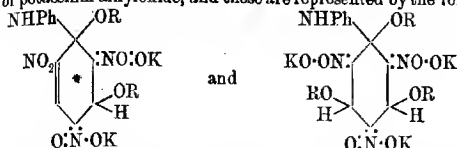
The dark modification of picric acid described by Georgievics (compare Abstr., 1906, i, 420) is shown to be ammonium picrate, formed by the absorption of ammonia from the air. W. H. G.

**Colour of Ammonium Picrate.** A. STEPANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 495—497).—By rapid crystallisation of an almost saturated solution, or by the action of gaseous ammonia on picric acid, a bright yellow ammonium picrate is obtained, the crystals being much smaller than those of the brownish-yellow variety, which is obtained on slower crystallisation; both modifications give a bright yellow powder (compare Silberrad and Phillips, *Trans.*, 1908, 83, 474). These two forms can be deposited in one and the same vessel by varying the rate of cooling, and show no sign of changing, one into the other, when left in this vessel for some months. Heating for some hours at 100° is likewise unaccompanied by interconversion of the two forms. At 170—180° part of the picrate volatilises, the crystals becoming corroded and assuming a yellow colour. The solutions of the two modifications are identical. The magnitude of the crystals is without influence on their colour, but in the powdered state the red and yellow forms are optically identical. Under the microscope, fragments of the crystals retain their transparency (compare Hantzsch, Abstr., 1906, i, 352, 353; 1907, i, 207, 500; Dimroth and Dienstbach, Abstr., 1909, i, 62; Korczyński, Abstr., 1909, i, 148). T. H. P.

**Salts of Aromatic Polynitro-compounds.** MAX BUSCH and WALTER KÖGEL (*Ber.*, 1910, 43, 1549—1564. Compare Sudborough and Picton, *Trans.*, 1906, 89, 593; Busch and Pungs, Abstr., 1909, i, 564).—The salts formed from compounds of the type of picrylaniline are not simple compounds:  $C_6H_2(NO_2)_3 \cdot NKPh$ , but are formed by the addition of potassium alkoxide to the nitro-compound, and are represented by quinonoid formulae, for example, the annexed constitution. Compounds of the type of picrylmethylaniline also yield similar salts, the only exception being picrylmethyl- $\alpha$ -naphthylamine, which appears to be incapable of forming salts. Picryl- $\alpha$ -naphthylamine forms a potassium salt which does not contain alcohol (compare Sudborough and Picton, *loc. cit.*).



The nitro-compounds can also form salts containing 2 or even 3 mols. of potassium alklyoxide, and these are represented by the formulæ:



The di-potassium compounds, as a rule, have not such a deep red colour as the mono-potassium salts, and the tri-potassium salts, which have a hexamethylene constitution, are pale yellow in colour.

*Picrylaniline potassium methoxide* (potassium 3:5-dinitro-4-anilino-4-methoxyquinolnitrosate),  $\text{C}_{13}\text{H}_{11}\text{O}_7\text{N}_4\text{K}$ , crystallises in glistening, black plates with a steel-blue lustre. It loses a molecule of methyl alcohol when heated at  $111^\circ$ , melts at  $115\text{--}120^\circ$ , and explodes at higher temperatures. The corresponding *ethyl* compound has m. p.  $115^\circ$ .

*Picrylaniline dipotassium ethoxide*,  $\text{C}_{16}\text{H}_{13}\text{O}_8\text{N}_4\text{K}_2$ , forms dark red crystals with no definite m. p., and the *tripotassium ethoxide*,  $\text{C}_{18}\text{H}_{23}\text{O}_9\text{N}_4\text{K}_3$ ,

forms a yellow, microcrystalline powder, which turns red when washed with alcohol.

*Picrylaniline potassium propoxide*, bluish-black plates, and the corresponding *dipotassium* compound have been prepared. With potassium hydroxide in isobutyl alcoholic solution, only the *tripotassium* salt,  $\text{C}_{24}\text{H}_{25}\text{O}_{10}\text{N}_4\text{K}_3$ , could be obtained as an orange-yellow precipitate.

*Picrylmethylaniline tripotassium ethoxide* is a reddish-brown amorphous powder. *Picrylmethylaniline dipotassium propylxide*,  $\text{C}_{16}\text{H}_{24}\text{O}_9\text{N}_4\text{K}_2$ , is similar.

*Picryl-β-naphthylamine potassium methoxide*,  $\text{C}_{17}\text{H}_{13}\text{O}_7\text{N}_4\text{K}$ , forms black needles, m. p.  $173^\circ$ , and is hydrolysed by water. The corresponding *ethoxide*,  $\text{C}_{18}\text{H}_{15}\text{O}_7\text{N}_4\text{K}$ , has m. p.  $168^\circ$ , and the *dipotassium isobutylxide*,  $\text{C}_{20}\text{H}_{19}\text{O}_7\text{N}_4\text{K}_2$ , is a pale red, amorphous compound.

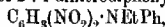
*Picryl-α-naphthylamine* is oxidised in alcoholic solution by an *N*-solution of silver nitrate to an orange-coloured, crystalline compound,  $\text{C}_{18}\text{H}_{10}\text{O}_8\text{N}_4$ , m. p.  $296\text{--}297^\circ$ .

*Picryl chloride* and *metbyl-α-naphthylamine* yield an additive compound,  $\text{C}_{17}\text{H}_{11}\text{O}_6\text{N}_4\text{Cl}$ , in the form of dark red, felted needles, m. p.  $94^\circ$ .

*Dibenzylpicramide*,  $\text{C}_{20}\text{H}_{16}\text{O}_8\text{N}_4$ , crystallises in yellow needles, m. p.  $173^\circ$ , and yields a potassium salt.

2:4-Dinitrodiphenylamine potassium methoxide,  $\text{C}_{18}\text{H}_{15}\text{O}_5\text{N}_3\text{K}$ , crystallises in violet-black, glistening needles, and the potassium isobutylxide,  $\text{C}_{18}\text{H}_{18}\text{O}_5\text{N}_3\text{K}$ , is similar.

The alkyl derivatives of 2:4-dinitrodiphenylamine, for example,



do not yield potassium salts, neither does dimethyl-2:4-dinitroaniline. Methyl-2:4-dinitroaniline yields an unstable, dark red potassium salt.

Trinitrobenzene yields a definite compound with 3 molecules potassium propylxide,  $C_{15}H_{24}O_9N_3K_3$ , which forms a red powder. Trinitrotoluene behaves in a similar manner.

J. J. S.

**Homochromoisomerism.** ARTHUR HANTZSCH (*Ber.*, 1910, 43, 1661—1662).—Chromoisomerides are substances which are chemically identical, but optically dissimilar, exhibiting differences in colour and absorption. The author describes a new kind of isomerism called homochromoisomerism. Homochromoisomerides are identical, not only chemically, but also optically, possessing the same colour, absorption, molecular extinction, and molecular refraction, but differ in m. p., solubility, etc. The only instances so far obtained are those of quinone-oximes and nitrated anilines.

[With JOSEPH LISTER.]—Picrylphenylmethylamine,  $C_6H_2(NO_2)_3NMePh$ ,

exists in two forms, each of which is unimolecular. The  $\alpha$ -form, m. p. 108—110°, has been obtained by Turpin (*Trans.*, 1891, 59, 716), and crystallises unchanged in dark red prisms from methyl or ethyl alcohol, acetic acid, ethyl acetate, ether, acetone, chloroform, carbon tetrachloride, carbon disulphide, and pyridine. The  $\beta$ -form, m. p. 128—129° (Sudborough and Pieton, *Trans.*, 1906, 89, 83), crystallises unchanged from benzene, acetonitrile, pyridine, or carbon disulphide. The  $\alpha$ -form is converted into the  $\beta$  at 100° or by crystallisation from benzene. The  $\beta$ -form is changed into the  $\alpha$  by crystallisation from methyl alcohol, ether, acetone, ethyl acetate, carbon tetrachloride, or chloroform. Both forms have identical absorption spectra, and practically identical molecular extinctions and molecular refractions (in pyridine).

$\alpha$ -Tolyl-2:4-dinitroanilino exists in two orange forms (and also in two yellow forms: compare following abstract), which are homochromoisomerides having the same absorption spectra, molecular extinctions, and molecular refractions.

[With R. FLADE.]—The *syn*- and the *anti*-modifications of quinone-oximes and also their salts are homochromoisomerides. The two forms of Kehrman's chlorotoluquinoneoxime have the same absorption spectra and molecular extinctions; the alcoholic solutions of their potassium salts have the same molecular extinctions, and aqueous solutions of the cesium salts have the same molecular refractions.

[With CURT B. HARTUNG.]—The preceding instance of homochromoisomerism has led to a more searching examination of the optical behaviour of other stereoisomeric oximes. *syn*- and *anti*-Benzilmonooximes are both colourless, and form yellow alkali salts, but their absorption spectra and molecular extinctions are different. The same is true of the stereoisomeric *p*-nitrobenzaloximes.

The difference in the optical behaviour of the *syn*- and the *anti*-modifications of benzilmonooxime and also of *p*-nitrobenzaloxime is probably due to the fact that the oximic hydroxyl is further removed from the unsaturated carbonyl or nitro-group in the *anti*- than in the *syn*-form; in the quinoneoximes the distance is the same in both

OH

modifications,  $O:C_6H_4MeCl:N$  and  $O:C_6H_4MeCl:N$ , and therefore the

OH

groups exert the same chemical and optical influence in both cases.

Homochromoisomerism, therefore, may represent an extreme case of stereoisomerism in which the mutual influence of unsaturated groups is not markedly affected by differences of configuration. C. S.

**Chromoisomerism and Homochromoisomerism of Nitroanilines.** ARTHUR HANTZSCH (*Ber.*, 1910, 43, 1662—1685).—A large number of nitrated anilines have been examined for the existence of differently coloured isomerides (chromoisomerides) or of similarly coloured isomerides (homochromoisomerides). Examples of the latter have been found only in picropheylmethanamide and in *o*-tolyl-2:4-dinitroaniline (preceding abstract), but instances of chromoisomerides are quite numerous in mono-, di-, and tri-nitroanilines containing mono- or di-substituted amino-groups.

The author develops his views at some length in a manner unsuitable for abstraction, and arrives at the following conclusions.

Nitrated anilines can exist in yellow, orange, and dark red forms; occasionally also in modifications having the same colour but different m. p. All these forms are unimolecular in solution. In one and the same solvent isomeric nitroanilines are optically identical, exhibiting the same absorption spectra, molecular refractions, and extinctions. Chromoisomeric nitroanilines contain chromophores of different constitution, whilst the constitutions of homochromoisomerides are explained on stereochemical grounds (preceding abstract). C. S.

**Peculiar Change Caused by Heating Salts of Phenolsulphonic Acids.** JULIUS OBERMILLER (*Ber.*, 1910, 43, 1413—1420).

—The melting of potassium *o*- and *p*-phenolsulphonates at 255—260° and 325—330° respectively are not cases of true fusion, but are caused by the decomposition of the salts with liberation of phenol. Thus potassium *o*-phenolsulphonate, when heated at a temperature not exceeding 300°, gives off about one-half of its phenol, and leaves an infusible residue consisting of potassium phenol-2:4-disulphonate containing a little phenol-2:4:6-trisulphonate. Other salts, such as the sodium, magnesium, and barium salts, which are infusible, behave in a similar way, only more slowly and at a higher temperature.

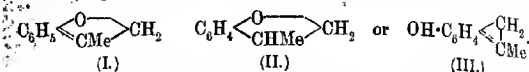
C. S.

**Structural Conditions Determining Anomalies in Boiling Points Among *o*-Substituted Phenols.** C. GUILLAUMIN (*Bull. Soc. chim.*, 1910, [iv], 7, 426—431).—It is known that phenols containing the group -CHO or -CO-OR in the ortho-position to the hydroxyl show anomalous boiling points; thus, *o*-hydroxybenzaldehyde, b. p. 196°, might be expected to boil at 245° (approx.), and methyl salicylate has b. p. 224°, instead of the expected value, 260°. Similar anomalous boiling points are shown by phenols containing the  $\psi$ -allyl side-chain in the ortho-position.

The author correlates these anomalies with (1) the presence of a free hydroxyl group, (2) the existence of an ortho-substituent possessing a double linking to the cyclic atom (carbon or nitrogen). It is possible



that such substances may at the point of ebullition pass into tautomeric forms of lower boiling point, and possible formulae for these are suggested; thus  $\psi$ -allyl- $\alpha$ -phenol might be represented by one of the following formulae:



No. II has a coumaran nucleus, and probably represents too stable a structure for this purpose. No. I would explain the lowering of boiling points in these compounds, but No. III has the advantage of being more readily applicable to the other cases mentioned, such as salicylaldehyde, methyl salicylate, etc.

T. A. H.

**Dehydrodicarvacrol.** HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1910, 150, 1333—1336).—Dehydrodicarvacrol,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{MePr}^2 \cdot \text{C}_6\text{H}_2\text{MePr}^2 \cdot \text{OH}$ , was obtained in an impure state by Dianine (Abstr., 1882, 623), and described under the name of  $\beta$ -thymol. It is best prepared as follows: Carvacrol (40 c.c.) is dissolved in 95% alcohol (400 c.c.), and poured into 100 litres of water. The liquid is shaken, filtered, and treated with 300 c.c. of ferric chloride solution (26%). After ten days the precipitate is collected, dissolved in alkali, reprecipitated by acetic acid, and crystallised from dilute alcohol, from which the compound separates in long, silky needles, m. p. 165—166°, containing  $2\text{H}_2\text{O}$ .

Dehydrodicarvacrol gives no coloration with ferric chloride. The dimethyl ether crystallises in small prisms, m. p. 110°; the diacetate forms lamellæ or felted needles, m. p. 182—183°; the dibenzoate occurs in long, prismatic needles, m. p. 185°.

W. O. W.

**Reduction with Metallic Calcium and Absolute Alcohol.** CHARLES MARSCHALK and FANNY NICOLAJEWSKY (*Ber.*, 1910, 43, 1700—1702. Compare this vol., i, 269).—By means of metallic calcium and absolute alcohol, benzoveratrole, veratroylveratrole, and veratroylquinol dimethyl ether are reduced to the corresponding leuco-compounds. Tetramethyl-*p*-diaminobenzophenone forms tetramethyl-*p*-diaminobenzhydrol. Naphthalene and anthracene yield dihydro-compounds; quinoline yields tetrahydroquinoline and an amorphous product. Pyridine yields ammonia and small quantities of a base with an odour like piperidine, indicating the opening of the ring; piperidine gives no ammonia.

E. F. A.

**cycloHexanetriols and their Derivatives.** LÉON BRUNEL (*Compt. rend.*, 1910, 150, 986—988. Compare Abstr., 1905, i, 869).—When an ethereal solution of ethoxy- $\Delta^2$ -cyclohexene is treated with iodine and mercuric oxide, an oily liquid is obtained having the composition  $\text{OEt} \cdot \text{C}_6\text{H}_9\text{I} \cdot \text{OH}$ , whilst if alcohol is used as the solvent, the composition of the product is represented by  $\text{C}_6\text{H}_9\text{I}(\text{OEt})_2$ .

Potassium hydroxide converts the first-mentioned iodo-derivative into an ether, b. p. 90—91°/25 mm., which, when heated with water, furnishes ethoxycyclohexane-2:3-diol,  $\text{OEt} \cdot \text{C}_6\text{H}_9(\text{OH})_2$ , b. p.

148—149°/20 mm. When this is hydrolysed by aqueous hydrobromic acid, a mixture of triols is obtained, which may be separated by fractional crystallisation of their acetates or benzoates.

$\alpha$ -cyclohexane-1:2:3-triol,  $C_6H_9(OH)_3$ , crystallises in needles, m. p. 108°; the triacetate forms prisms, m. p. 126° with sublimation; the tribenzoate occurs in long needles, m. p. 141—142°.  $\beta$ -cyclohexane-1:2:3-triol, m. p. 124°, forms a syrupy triacetate and a tribenzoate crystallising in large prisms, m. p. 181°. The  $\beta$ -compound is formed in larger proportion and free from the  $\alpha$  isomeride by oxidising ethoxycyclo- $\Delta^2$ -hexane with alkaline permanganate and treating the product, ethoxycyclohexane-2:3-diol, with hydrobromic acid. W. O. W.

Phenols of the Type  $OH \cdot C_6H_3Me \cdot CMe \cdot CH_2$  with  $\psi$ -Allyl Side-chains. I.  $\psi$ -Allyl-*o*-cresol. II.  $\psi$ -Allyl-*m*-cresol. III.  $\psi$ -Allyl-*p*-cresol. C. GUILLAUMIN (*Bull. Soc. chim.*, 1910, [iv], 7, 374—383).—The synthesis of the methyl ethers of these  $\psi$ -allyl phenols has been described already (Béhal and Tiffeneau, *Abstr.*, 1908, i, 630, and this vol., i, 374; Guillaumin, this vol., i, 375). In this paper an account is given of the application of analogous methods to the preparation of the three isomeric phenols and their derivatives.

Methyl *o*-hydroxytoluate,  $D^{16} 1.1683$ ,  $D^{18} 1.1529$ ,  $n_D^{18} 1.53538$ , m. p. -0.5°, b. p. 237—239°/760 mm. or 119—121°/14 mm. (corr.), furnishes with magnesium methyl iodide (3.5 mols.) *o*-hydroxytolyl-dimethylcarbinol,  $OH \cdot C_6H_3Me \cdot CMe_2 \cdot OH$  [2:1:3], m. p. 75.5°, b. p. 140—144°/14 mm. (corr.), which forms colourless crystals from benzene, and when heated decomposes at 208—213°, yielding an unsaturated hydrocarbon; when heated with acetic anhydride during twelve hours it furnishes *o*-acetoxy- $\psi$ -allyltoluene,

$OAc \cdot C_6H_3Me \cdot CMe \cdot CH_2$   
[2:1:3],  $D^{16} 1.0357$ , h. p. 236—238°/760 mm. or 115—116°/13 mm. (corr.), a colourless liquid, which gradually becomes green and decolorises bromine or potassium permanganate. On hydrolysis with potassium hydroxide in alcohol, this acetate furnishes  $\psi$ -allyl-*o*-cresol,  $OH \cdot C_6H_3Me \cdot CMe_2 \cdot CH_2$  [2:1:3],  $D^{16} 1.0143$ ,  $D^{18} 0.9980$ ,  $n_D^{18} 1.54193$  (compare Béhal and Tiffeneau, *loc. cit.*).

The following meta-isomerides of the above substances were prepared from methyl *m*-hydroxytoluate,  $D^{16} 1.1621$ ,  $D^{18} 1.1483$ ,  $n_D^{18} 1.53781$ , b. p. 242—244°/760 mm. (corr.) (compare *Abstr.*, 1908, i, 630). *m*-Hydroxytolyl-dimethylcarbinol, m. p. 64°, b. p. 140—143°/14 mm. (corr.) (compare Fries and Fickewirth, *Abstr.*, 1908, i, 824), with acetic anhydride yields the corresponding *m*-acetoxy- $\psi$ -allyltoluene,  $D^{16} 1.0358$ ,  $D^{18} 1.0238$ ,  $n_D^{18} 1.51790$ , b. p. 122—123°/764 mm. (corr.), a colourless liquid which becomes lemon-yellow after several days. On hydrolysis this acetate yields  $\psi$ -allyl-*m*-cresol,  $D^{16} 1.0241$ ,  $D^{18} 1.0130$ ,  $n_D^{18} 1.55329$ , b. p. 221—222°/758 mm. or 106—107°/13 mm. (corr.), a colourless liquid giving a green coloration with ferric chloride (compare Fries and Fickewirth, *Abstr.*, 1908, i, 160). It condenses with chloroacetic acid, forming  $\psi$ -allyl-*m*-tolylglyoxyacetic acid, m. p. 112°, which crystallises from aqueous alcohol in colourless needles, and polymerises rapidly on distillation at atmospheric pressure.

The following para-isomerides were prepared in like manner from

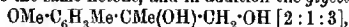
methyl *p*-hydroxytoluate,  $D^0$  1.1673,  $D^{155}$  1.1534,  $n_D^{155}$  1.53514, m. p.  $-1^\circ$ , b. p.  $241-243^\circ/767$  mm. or  $122-124^\circ/14$  mm. (corr.): *p*-Hydroxytolylidimethylcarbinol, m. p.  $81^\circ$ , b. p.  $144-148^\circ/14$  mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 824). *p*-Acetoxy- $\psi$ -allyltoluene,  $D^0$  1.0383, b. p.  $244-246^\circ/763$  mm. or  $129.5-131.5^\circ/13$  mm. (corr.), is a colourless liquid, which becomes orange-red after a few hours.  $\psi$ -Allyl-*p*-cresol,  $D^0$  1.0285,  $D^{155}$  1.0177,  $n_D^{155}$  1.54987, b. p.  $220-222^\circ/760$  mm. (corr.) (compare Fries and Fickewirth, Abstr., 1908, i, 160). When condensed with chloroacetic acid, it furnishes  $\psi$ -allyl-*p*-tolylacetic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{CMe}\cdot\text{CH}_2$  [2:5:1], m. p.  $97^\circ$ , which crystallises in long, colourless needles from boiling alcohol, and is slightly soluble in cold, more so in hot water, and very soluble in ether.

The author was unable to obtain the crystalline polymerides of  $\psi$ -allyl-*m*-cresol and of its *p*-isomeride described by Fries and Fickewirth (*loc. cit.*). T. A. H.

**Phenylic Transposition of  $\psi$ -Allyl Phenyl Ethers Derived from *o*- or *p*-Cresol.** C. GUILLAUMIN (*Bull. Soc. chim.*, 1910, [iv] 7, 420-426).—It has been shown previously that the iodohydrins of aromatic compounds containing  $\psi$ -allyl side-chains, when treated with silver nitrate or yellow mercuric oxide, are transformed into derivatives

of acetone, thus:  $\text{Ar}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{I} \rightarrow \text{Ar}\cdot\text{CH}_2\cdot\text{COMe}$  (Tiffeneau, Abstr., 1907, i, 304; 1908, i, 165, 166). It is now shown that a like transposition is brought about by the action of moist silver oxide on the iodohydrin, but that in this case the iodine atom is, in part, normally replaced by an -OH group, giving rise to the corresponding glycol, thus:  $\text{Ar}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\text{I} \rightarrow \text{Ar}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ . The substances studied so far indicate (1) that "steric hindrance" plays no part in preventing the transposition of the aromatic radiæ in the first action, and (2) that in the transposed aromatic radiæ no change in the positions of substitution occurs.

2-Methoxy-1-methyl-3- $\psi$ -allylbenzene (this vol., i, 375), on treatment with iodine and yellow mercuric oxide in ether, gives an iodohydrin, which with silver nitrate furnishes 2-methoxy-1-methyl-3-acetylbenzene,  $D^0$  1.0571, b. p.  $257-259^\circ/763$  mm. (corr.); the sodium hydrogen sulphite compound of this is readily dissociated by water; the semicarbazone, recrystallised from benzene, separates into two fractions, m. p.  $169^\circ$  and  $171^\circ$  respectively. With moist silver oxide the iodohydrin yields the same ketone, and in addition the glycol,



b. p.  $200-220^\circ/13$  mm.,  $D^0$  1.1100, a viscous liquid, which on distillation at atmospheric pressure furnishes the corresponding aldehyde,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHMe}\cdot\text{CHO}$  [2:1:3].

4-Methoxy-1-methyl-3- $\psi$ -allylbenzene furnishes an iodohydrin, which on treatment with silver nitrate yields 4-methoxy-1-methyl-3-acetylbenzene, b. p.  $266-267^\circ/75$  mm. (corr.),  $D^0$  1.0583,  $D^{155}$  1.0460,  $n_D^{155}$  1.52324, a colourless liquid, which combines with sodium hydrogen sulphite only when pure, and in concentrated solution in ether; the semicarbazone, m. p.  $150^\circ$ , crystallises from benzene. T. A. H.

Conversion of Hydroaromatic Alcohols into the Corresponding Phenols. LÉON BRUNEL (*Compt. rend.*, 1910, 150, 1528—1530).—To ascertain whether the side-chain undergoes any change during the direct hydrogenation of thymol by the method already described (Abstr., 1905, i, 197), the author has oxidised the product, thymomenthol, with chromic acid, and brominated the thymomenthone so formed. *Dibromothymomenthone*,  $C_{10}H_{16}OBr_2$ , crystallises in large prisms, m. p.  $97^\circ$ , and on heating with quinoline furnishes thymol identical with the starting material. Thymol was also formed on submitting menthol or thymomenthol to catalytic dehydrogenation in presence of reduced copper at  $230$ – $240^\circ$ . Under the same conditions, carvomenthol (Abstr., 1906, i, 81) was converted into carvacrol, an unsaturated hydrocarbon,  $C_{10}H_{18}$ , b. p.  $174$ – $176^\circ$ , being formed as a by-product. The corresponding hydrocarbon from menthol or thymomenthol had b. p.  $166$ – $168^\circ$ . W. O. W.

Simple Formation of Benzyl Ethers. JULIUS VON BRAUN (*Ber.*, 1910, 43, 1350—1352).—Compounds such as benzyl bromide and *o*-xylyl bromide, when boiled with dilute sulphuric acid and alcohol, or even with dilute alcohol, have the bromine replaced by the alkoxy-group, and ethers are formed.

In this way the following have been prepared: Benzyl methyl ether, b. p.  $174^\circ$  (previously given as  $167$ – $171^\circ$ ); benzyl ethyl ether, b. p.  $189^\circ$  (previously given as  $185$ – $186^\circ$ ); *o*-xylyl ethyl ether, b. p.  $208$ – $210^\circ$ , which has an odour like peppermint; benzyl allyl ether, b. p.  $204$ – $205^\circ$ , which has a pleasant ethereal odour; at the same time a compound, which is not volatile in steam, h. p.  $150$ – $152/9$  mm., is obtained.

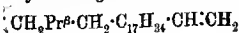
Benzyl bromide also reacts with glycol and glycerol, but a mixture of products is formed. Phenylethyl bromide does not react with alcohol in this manner. E. F. A.

Aminoaryl Alcohols. II. Formation of a Phenylglycol from the Ammonium Base of  $\alpha$ -Amino- $\alpha$ -phenylisopropyl Alcohol. HERMANN EMDE and ERNST RUNNE (*Ber.*, 1910, 43, 1727—1729. Compare Abstr., 1909, i, 300).—The quaternary ammonium base derived from  $\alpha$ -amino- $\alpha$ -phenylisopropyl alcohol when warmed in aqueous solution is decomposed into trimethylamine and the  $\beta$ -form of  $\alpha$ -phenylpropylene  $\alpha\beta$  glycol (compare Zincke, Abstr., 1884, 1003; Zincke and Zahn, this vol., i, 316). The quaternary base contains two asymmetric carbon atoms, but fractional crystallisation of the following salts did not lead to any separation of the isomerides.

The iodide,  $NMe_3I \cdot CHPh \cdot CHMe \cdot OH$ , forms hard, short crystals, m. p.  $176$ – $177^\circ$ . The chloride,  $+H_2O$ , crystallises in transparent, long plates, m. p.  $138$ – $139^\circ$ , or when anhydrous, m. p.  $196$ – $197^\circ$ . The platinumchloride crystallises well, decomp.  $233$ – $234^\circ$ ; the aurichloride forms long, single needles, m. p.  $151.5^\circ$ , decomp.  $220^\circ$ . E. F. A.

Derivatives of Cholesterol. LEO TSCHUGAEFF and W. FOMIN (*Compt. rend.*, 1910, 150, 1435—1437. Compare this vol., i, 31).—Cholesterylene, previously obtained by the decomposition of methyl

cholesterylzanthate, has now been separated by crystallisation from ether and alcohol into two isomeric hydrocarbons:  $\alpha$ -cholesterylene, crystallising in needles, m. p.  $77^\circ$ ,  $[\alpha]_D - 109.3^\circ$  in toluene, and  $\beta$ -cholesterylene, m. p.  $59^\circ$ ,  $[\alpha]_D - 76.68^\circ$ , in toluene solution. Both compounds



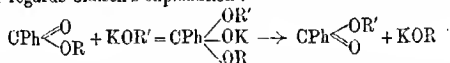
show normal rotatory dispersion. When treated with hydrogen in presence of platinum-black, they yield the same hydrocarbon, cholestane, identical with that obtained from cholestene by Mauthner (Abstr., 1909, i, 714).

The annexed constitution is suggested for cholesterylene, the two modifications being supposed to differ in the position of the double linking in the ring.

W. O. W.

**Interchange of Alkyl Groups in Esters of Organic Acids.** MICHAEL PFANNL (*Monatsh.*, 1910, 31, 301—317).—It has long been known that the alkyl group of an ester can be exchanged for another alkyl group by means of sodium or an alkali hydroxide dissolved in the alcohol corresponding with the second alkyl group. By means of experiments on the methyl, ethyl, and propyl esters of terephthalic acid, of benzoic acid, and of oxalic acid, the author shows that the exchange is quite general, and is completely reversible. The method consists in dissolving a known quantity of an ester in at least ten times the amount of an alcohol, and adding in the cold a quantity of potassium hydroxide or of sodium dissolved in the alcohol in question; the exchange proceeds to completion at the ordinary temperature in a time, thirty minutes to fifteen hours, depending on the amount of alkali present, the greater the amount of alkali the shorter the time required; the alkali is then neutralised, water is added, and the new ester is removed by ether or by filtration.

The velocity of the exchange is directly proportional to the quantity of alkali present; consequently Kremann's theory that the alkali acts merely as a catalyst (Abstr., 1908, i, 120) must be incorrect. The author regards Claisen's explanation:



as affording the best interpretation of the results, for it explains (i) the reversibility of the exchange, (ii) the absence of any exchange in the absence of alkali, (iii) the absence of any exchange in the case of substances, such as phenolic ethers, which are unable to aid on potassium alkyl oxide, (iv) the proportionality between the velocity of the exchange and the concentration of the alkali.

C. S.

**cycloHexylglycollic Acid.** MARCEL GODCHOT and JULES FREZOULS (*Compt. rend.*, 1910, 150, 1248—1250. Compare Zelinsky and Schwedoff, Abstr., 1908, i, 864).—cycloHexylglycollonitrile undergoes decomposition when distilled; hydrochloric acid converts it into the *amide*, crystallising in pearly leaflets, m. p.  $155^\circ$ . The free acid obtained by the hydrolysis of the amide with alkalis occurs as

prismatic needles, m. p. 130—131°; the sodium and silver salts have been analysed. In the authors' opinion, the acid described under this name by Zelinsky and Schwedoff was a mixture. W. O. W.

[Preparation of Isomeric Nitrobenzoyl Derivatives of Nitroanilines, Nitrotoluidines, and their Reduction Products.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 221433).—An account of the preparation of dyes from tetrazotised compounds, of the general formula  $\text{NH}_2 \cdot \text{R} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$  (R = an aromatic nucleus) combined with two molecules of various naphtholsulphonic acids.

The following initial compounds are mentioned, and were prepared by the usual methods: *m*-Nitrobenzoyl-*p*-nitroaniline, yellow powder, m. p. 249°. *m*-Aminobenzoyl-*p*-phenylenediamine, brown needles, m. p. 150°. *p*-Nitrobenzoyl-*p*-nitroaniline, yellow, crystalline powder, m. p. 266°. *p*-Aminobenzoyl-*p*-phenylenediamine, brown needles, m. p. 205°, soluble in hot water. *m*-Nitrobenzoyl-*m*-nitroaniline, brown needles, m. p. 185°. *m*-Aminobenzoyl-*m*-phenylenediamine, m. p. 130°. *p*-Nitrobenzoyl-*m*-nitroaniline, yellow needles, m. p. 227°. *p*-Aminobenzoyl-*m*-phenylenediamine, grey powder, m. p. 173°. *m*-Nitrobenzoyl-*p*-nitro-*o*-toluidine, colourless, glistening leaflets, m. p. 193°. *m*-Aminobenzoyl-*m*-tolylenediamine, brown, crystalline powder, m. p. 177°. *p*-Nitrobenzoyl-*p*-nitro-*o*-toluidine, brownish-yellow needles, m. p. 214°.

F. M. G. M.

**Bromination of Anthranilic Acid.** ALVIN S. WHEELER and W. M. OATES (*J. Amer. Chem. Soc.*, 1910, 32, 770—773).—A study has been made of the action of bromine on anthranilic acid dissolved in glacial acetic acid, both near the m. p. of the acetic acid and also near its b. p. In the former case the product consists of 5-bromo-2-aminobenzoic and 3:5-dibromo-2-aminobenzoic acids in the proportion of 2:1, whilst in the latter case the proportions are almost exactly reversed.

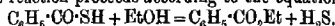
The silver salt and ethyl ester, m. p. 187°, of 5-bromo-2-aminobenzoic acid are described. 5-Bromoacetylaurhanil has m. p. 134° (compare Bogert and Hand, *Abstr.*, 1906, i, 176). 3:5-Dibromoacetylaurhanil, m. p. 176°, forms long, colourless needles. 3:5-Dibromoacetyl-2-aminobenzoic acid, m. p. 218—219°, obtained by boiling the anil with dilute sodium hydroxide or with glacial acetic acid, crystallises in microscopic needles; its silver salt decomposes at about 270°, and its ethyl ester has m. p. 74°.

E. G.

**Esterification.** Esterification of Thiolbenzoic Acid by Alcohol and of Benzoic Acid by Mercaptan. E. EMMET REID (*Amer. Chem. J.*, 1910, 43, 489—504).—In accordance with Henry's hypothesis, the esterification of thiolbenzoic acid by alcohol should take place as follows:  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{SH} + \text{EtOH} \rightleftharpoons \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH})(\text{SH}) \cdot \text{OEt}$ , and this additive compound may break up into  $\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et} + \text{H}_2\text{S}$  or into  $\text{C}_6\text{H}_5 \cdot \text{CS} \cdot \text{OEt} + \text{H}_2\text{O}$ . In the esterification of benzoic acid by mercaptan, the reaction would be in accordance with the equation:  $\text{C}_6\text{H}_5 \cdot \text{CO}_2\text{H} + \text{EtSH} \rightleftharpoons \text{C}_6\text{H}_5 \cdot \text{C}(\text{OH})_2 \cdot \text{SEt} \rightleftharpoons \text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{SEt} + \text{H}_2\text{O}$ .

Qualitative and quantitative experiments have been carried out in order to study these reactions, and to ascertain the mode and extent of esterification of mercaptan.

It has been found that when hydrogen chloride is passed into a solution of thiolbenzoic acid in alcohol, hydrogen sulphide and ethyl benzoate are produced, but ethyl thionbenzoate does not seem to be formed. The reaction proceeds according to the equation:



The same change takes place in the absence of a catalytic agent when thiolbenzoic acid and alcohol are heated in a sealed tube at about  $150^\circ$ . The reaction is not reversible. Thiolbenzoic acid is not produced by the action of hydrogen sulphide on ethyl benzoate, but benzoic acid and mercaptan are obtained thus:  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{Et} + \text{H}_2\text{S} = \text{C}_6\text{H}_5\cdot\text{CO}_2\text{H} + \text{EtSH}$ .

Mercaptan has the power of forming esters, both in presence and absence of a catalytic agent, but is less efficient than alcohol. The reaction between benzoic acid and mercaptan is reversible, and is expressed by the equation:  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H} + \text{EtSH} = \text{C}_6\text{H}_5\cdot\text{CO}_2\text{SEt} + \text{H}_2\text{O}$ . It obeys the law of mass action, and a true equilibrium is reached with about 16.8 per cent. of esterification. E. G.

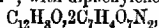
**Synthesis of Aromatic Nitriles.** F. BODROUX and FELIX TABOURY (*Compt. rend.*, 1910, 150, 1241—1243. Compare this vol. i, 257).—Nitriles of the type  $\text{CHPhR}\cdot\text{CN}$  condense with alkyl halides in the presence of sodamide, giving nitriles of the type  $\text{CPhRR}\cdot\text{CN}$ . The following compounds have been prepared in this way: *α*-phenyl-*α*-ethylbutyronitrile,  $\text{CEt}_2\text{Ph}\cdot\text{CN}$ , h. p.  $125.5-127^\circ/13$  mm.,  $247-249^\circ/752$  mm.,  $D^{16}_D$  0.957; *α*-phenyl-*γ*-methyl-*α*-isopropylvaleronitrile,  $\text{CH}_3\text{Pr}^i\text{CPr}^i\text{Ph}\cdot\text{CN}$ ,

b. p.  $148-150^\circ/15$  mm.,  $D^{16}_D$  0.932. Similar compounds have also been prepared by the direct action of alkyl halides on phenylacetonitrile in presence of sodamide; thus *n*-propyl bromide furnishes *α*-phenyl-*α*-*n*-propylvaleronitrile,  $\text{CPr}^n\text{Ph}\cdot\text{CN}$ , h. p.  $142.5-145^\circ/15$  mm.,  $268-270^\circ/758$  mm.,  $D^{14}_D$  0.940; isobutyl bromide yields *α*-phenyl-*γ*-methyl-*α*-isobutylvaleronitrile,  $\text{C}(\text{CH}_2\text{Pr}^i)_2\text{Ph}\cdot\text{CN}$ , h. p.  $152-155^\circ/15$  mm.,  $D^{13}_D$  0.931. W. O. W.

**Compounds of 3:5-Dinitro-4-hydroxybenzoic Acid with Hydrocarbons.** OTTO MORGENSEN (*Monatsh.*, 1910, 31, 285—294).—3:5-Dinitro-4-hydroxybenzoic acid, the ammonium salt of which exists in a yellow and a red modification, resembles picric acid in forming coloured compounds with aromatic hydrocarbons. The following compounds are described: with acenaphthene,



m. p.  $210-211^\circ$  (decomp.), reddish-orange needles; with naphthalene,  $\text{C}_{10}\text{H}_8\cdot\text{C}_7\text{H}_4\text{O}_7\text{N}_2$ , m. p.  $214-217^\circ$  (in closed tube), yellow needles; with pyrene,  $\text{C}_{16}\text{H}_{10}\cdot\text{C}_7\text{H}_4\text{O}_7\text{N}_2$ , m. p.  $251-252^\circ$  (decomp.), orange-red needles; with fluorene,  $\text{C}_{13}\text{H}_{10}\cdot 2\text{C}_7\text{H}_4\text{O}_7\text{N}_2$ , m. p.  $218-221^\circ$ , pale yellow powder; with retene,  $\text{C}_{18}\text{H}_{18}\cdot 2\text{C}_7\text{H}_4\text{O}_7\text{N}_2$ , pale yellow leaflets decomposing at  $229-231^\circ$ ; with diphenylene oxide,



m. p. 226—232° (decomp.), pale yellow needles; with phenanthrene,  $C_{14}H_{10}$ ,  $2C_7H_5O_2N_2$ , m. p. 218—222°, reddish-yellow needles; with quinoline,  $C_9NH_7$ ,  $C_7H_5O_2N_2$ , citron-yellow powder decomposing at 224.5—225°.

All these compounds are prepared by mixing alcoholic solutions of the constituents and subsequently concentrating the mixture, if necessary; they are more or less unstable, and are partly decomposed by recrystallisation from alcohol, and completely by benzene at the ordinary temperature. C. S.

**Lactonoid Anhydrides of Acylated Amino-acids. III. The Lactone of *r*-Benzoylalanine and its Application for the Synthesis of Benzoylated Dipeptides.** ERNST MOHR [with FR. SPROSCHKEIN] (*J. pr. Chem.*, 1910, [ii], 81, 473—500. Compare this

vol. i, 116, 117).—The lactone,  $CHMe \begin{smallmatrix} \nearrow N=CPh \\ \searrow CO \cdot O \end{smallmatrix}$ , m. p. 39—39.5°, of

*r*-benzoylalanine is obtained by heating finely powdered benzoylalanine and acetic anhydride on the water-bath for not more than ten minutes, removing the acetic acid formed and the excess of the anhydride under 0.2—0.5 mm. pressure, and finally distilling the lactone, which passes over at 75—140°/0.2—0.5 mm., and crystallises by keeping in a vacuum desiccator. The lactone develops a temporary intense bluish-violet fluorescence on treatment with *N*/10-sodium hydroxide, and in its chemical behaviour resembles the lactone of benzoyl- $\alpha$ -aminoisobutyric acid. It easily yields benzoylalanine with hot water, benzoylalanine-amide with ethereal ammonia, ethyl benzoylalanine with alcohol, benzoylalananyl chloride with cold ethereal hydrogen chloride, and Curtius and van der Linden's benzoylalanineanilide with ethereal aniline. Whether prepared in this way or from ethyl benzoylalanine and aniline, or from benzoylalananyl chloride and aniline, the anilide has m. p. 176—176.5°, not 163—165° as given by these authors (*Abstr.*, 1904, i, 883).

Curtius and van der Linden's benzoylalananylglycine (*loc. cit.*) is obtained by adding the lactone to aqueous glycine, keeping the mixture faintly alkaline during the reaction, and subsequently acidifying with 10*N*-hydrochloric acid. In a similar manner, benzoylalananylalanine is obtained from *r*-alanine, and benzoylalananyl- $\alpha$ -aminoisobutyric acid,  $NHBz \cdot CHMe \cdot CO \cdot NH \cdot CMe_2 \cdot CO_2H$ , m. p. 199—199.5°, from  $\alpha$ -aminoisobutyric acid. By heating with acetic anhydride, the last benzoylated dipeptide alone yields a lactone,  $NHBz \cdot CHMe \cdot C \begin{smallmatrix} \nearrow N \cdot CMe_2 \\ \searrow O \cdot CO \end{smallmatrix}$ , m. p. 116—117°, which reacts with ethereal ammonia at 0° to form benzoylalananyl- $\alpha$ -aminoisobutyramide, m. p. 209°.

A comparison is drawn between the properties of benzoyl- $\alpha$ -aminoisobutyric acid, benzoylalanine, and hippuric acid. The last stands somewhat apart from the first two, being most easily decomposed, but the amide of the first yields a cyclic imide with boiling dilute sodium hydroxide, whilst the amides of the second and the last undergo normal hydrolysis. C. S.



**Reaction between Unsaturated Compounds and Organic Zinc Compounds.** ELMER P. KOHLER and GERTRUDE L. HERITAGE (*Amer. Chem. J.*, 1910, 43, 475—489).—It has been stated by Kohler and Burnléy (this vol., i, 391) that the relation between the character of organic magnesium compounds and their mode of addition to ketones containing the chain  $C=C:O$  is not easily determined. The results of earlier work show that magnesium compounds containing alkyl groups behave differently from those derived from aromatic compounds which have the halogen directly attached to the nucleus. The former give almost the same amount of the 1:4-additive product with any one ketone, whilst magnesium phenyl bromide and magnesium tolyl bromide give relatively a much larger quantity of the 1:2-additive product. Attempts have been made to find an explanation for this difference. Owing to certain difficulties which arose, it was decided to substitute zinc for magnesium, and experiments are now described on the action of methyl bromoacetate and zinc on benzylidenacetophenone, benzylidenepropiophenone, and other unsaturated compounds. These ketones give only saturated compounds with the ordinary Grignard reagents, but have been found to yield unsaturated  $\beta$ -hydroxy-esters when they react with zinc and methyl bromoacetate. It has been proved that this difference does not depend on the metal, solvent, or procedure, but is due entirely to the nature of the halogen compounds used.

When a solution of benzylidenacetophenone in benzene is heated with methyl bromoacetate and a slight excess of zinc, 1:2-addition takes place with formation of *methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\gamma$ -benzylidenobutyrate*,  $CHPh:CH-CPh(OH) \cdot CH_2 \cdot CO_2Me$ , m. p. 126°, which crystallises in slender needles. This ester combines with bromine to form a solid dibromide, which on recrystallisation from chloroform is converted into *methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\gamma$ -bromobenzylidenobutyrate*,  $CPhBr:CH-CPh(OH) \cdot CH_2 \cdot CO_2Me$ , which forms thick needles, and begins to decompose at about 200°. Magnesium can be used instead of zinc in the reaction between benzylidenacetophenone and methyl bromoacetate, and, in this case, as in the former, only the 1:2-additive compound is produced. When magnesium is employed, ether can be used instead of benzene as a solvent, but the manipulation is troublesome and the yield unsatisfactory.

*Methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\gamma$ -benzylidenovalerate*,  
 $CHPh:CH-CPh(OH) \cdot CH_2 \cdot CO_2Me$ ,  
 m. p. 70°, obtained by the action of methyl bromoacetate on benzylidenepropiophenone in presence of zinc and benzene, or magnesium and ether, forms large, lustrous plates.

When ethylidenacetophenone is treated with methyl bromoacetate and zinc, *methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\Delta^7$ -hexenoate*,  
 $CHMe:CH-CPh(OH) \cdot CH_2 \cdot CO_2Me$ ,  
 m. p. 58°, is produced, which crystallises in long needles; its bromo-derivative,  $CMeBr:CH-CPh(OH) \cdot CH_2 \cdot CO_2Me$ , m. p. about 175° (decomp.), forms small prisms or plates.

Cinnamaldehyde, when treated in the same way, gives a product which does not solidify, but, on distillation under reduced pressure, loses water and yields methyl cinnanylideneacetate. This aldehyde

reacts similarly with methyl  $\alpha$ -bromopropionate to form methyl  $\alpha$ -methylcinnamylidenacetate.

*Ethyl  $\beta$ -hydroxy- $\beta$ -methyl- $\gamma$ -benzylidenobutyrate,*  
 $\text{CHPh}\cdot\text{CH}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et},$

b. p.  $192^\circ/20$  mm., obtained from styryl methyl ketone and ethyl bromoacetate, is a colourless liquid, and on hydrolysis with potassium hydroxide yields phenylmethylbutadiene, m. p.  $37^\circ$ . When this ester is boiled with hydrochloric acid, it is converted into  $\beta$ -methylcinnamylidenacetic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , m. p.  $153^\circ$ , which forms small prisms or plates.

The product obtained from benzylidenepinacoln and methyl bromoacetate loses water on distillation under reduced pressure, and yields methyl  $\beta$ -butylcinnamylidenacetate, b. p.  $210^\circ/20$  mm.

*Methyl  $\gamma$ -bromo- $\beta$ -hydroxy- $\beta$ -phenyl- $\gamma$ -benzylidenobutyrate,*  
 $\text{CHPh}\cdot\text{CBr}\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me},$

m. p.  $79-80^\circ$ , prepared from  $\alpha$ -bromobenzylidenacetophenone and methyl bromoacetate, forms colourless needles.

Cinnamylidenacetophenone reacts with methyl bromoacetate to form methyl  $\beta$ -hydroxy- $\beta$ -phenyl- $\gamma$ -cinnamylidenobutyrate,

$\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me},$

m. p.  $112^\circ$ , which crystallises in slender needles.

Benzylidenedeoxybenzoin and benzylidenecetylmesitylene do not react with methyl bromoacetate in presence of zinc, although they readily give 1 : 1 additive compounds with Grignard reagents.

E. G.

**Preparation of Iodoacetylsalicylic (*o*-Iodoacetyloxybenzoic) Acids.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.P. 221384).—The *o*-bromoacetyloxybenzoic acids have been previously described (Abstr., 1909, i, 798); it is now found that *o*-iodoacetyloxybenzoic acids can be readily prepared by similar methods, and are of therapeutic value as antirheumatics.

*o*-Iodoacetyloxybenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{I}$ , obtained by the interaction of iodoacetyl chloride and sodium salicylate in dry benzene solution, forms colourless needles, m. p.  $138^\circ$  (decomp.).

*o*-*a*-Iodoisovaleryloxybenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CHI}\cdot\text{CHMe}_2$ , colourless crystals, m. p.  $102^\circ$ , is analogously prepared.

F. M. G. M

**Piperonylic Acid.** E. OERTLY and ANÉ PICTET (*Ber.*, 1910, 43, 1336—1340).—*Methyl piperonylate*,  $\text{CH}_3\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}_2\text{Me}$ , forms colourless needles, m. p.  $53^\circ$ . The *mononitro*-derivative, obtained by interaction with fuming nitric acid and acetic acid, crystallises in colourless needles, m. p.  $103^\circ$ , and on reduction by means of tin chloride and acetic acid is converted into *methyl aminopiperonylate*, which separates in silver-grey needles, m. p.  $108^\circ$ . On replacing the amino-group by carboxyl, hydrastie acid is obtained, showing the amino-group to be in position 6.

*Methyl cyanopiperonylate* is prepared by diazotising the amino-compound in hydrochloric acid solution and adding potassium cyanide, and crystallises in light yellow needles, m. p.  $135-136^\circ$ . Hydrolysis con-

verts this into hydrastic acid, and this affords a convenient process for preparing this acid. Nitration of methyl hydrastate gives the nitro-compound already described.

The position of the bromine atom in bromopiperonal and bromopiperonylic acid (Fittig and Mielch, *Annalen*, 1869, 152, 49) was unknown previously. The latter compound yields a methyl ester separating in colourless crystals, m. p. 87–88°, which substance is also obtainable from methyl aminopiperonylate by diazotisation and decomposition with copper bromide. This fixes position 6 as that of the bromine atom.

*Bromonitrocatechol methylene ether*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)\text{Br}$ , crystallises in yellow needles, m. p. 87°.

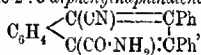
*Methyl bromonitropiperonylate*,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}(\text{NO}_2)\text{Br}\cdot\text{CO}_2\text{Me}$ , forms yellow needles, m. p. 131°, and on reduction with ammonium sulphide is converted into *methyl bromoaminopiperonylate*, which separates in greyish-white needles, m. p. 92°.

E. F. A.

**Synthetical Experiments with o-Xylylene Cyanide.** OSCAR HINSBERG (*Ber.*, 1910, 43, 1360–1363).—o-Xylylene cyanide contains two reactive methylene groups, and therefore condenses in presence of sodium ethoxide with o-diketones, keto-acids, and esters of oxalic acids to naphthalene derivatives.

With ethyl oxalate, 1:4-dicyano-2:3-dihydroxynaphthalene is formed; this crystallises in a voluminous mass of light yellow plates, m. p. 291°, and shows an intense blue coloration with ferric chloride.

With benzil, 1-cyano-2:3-diphenylnaphthalene-4-carboxylamide,



is formed; this separates in colourless crystals, m. p. above 290°.

With phenanthraquinone, cyanonaphthalphenanthrene-carboxylamide is obtained, crystallising in minute, yellow needles, m. p. 306°. Hydrolysis of these substances to the corresponding carboxylic acids does not take place easily.

E. F. A.

**Preparation of Alkyl- and Aryl-oxyacetylsalicylic [o-Aryl-oxyacetoxybenzoic] Acids.** CHEMISCHE FABRIK VON FRIEDR. HEIDEN (D.R.-P. 221335).—The o-alkyl- and o-aryl-oxyacetylbenzoic acids are prepared by the action of the anhydrides, or alkyl- or aryl-oxyparaffin acid chlorides on salicylic acid in the presence or absence of condensing agents.

*o-Phenoxyacetoxybenzoic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OPh}$ , tasteless, colourless needles, m. p. 143°, is prepared by slowly adding phenoxyacetyl chloride to a suspension of sodium salicylate in benzene at 16° with continual stirring during seven hours.

*o-Ethoxyacetoxybenzoic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OEt}$ , colourless needles, m. p. 91°, is analogously prepared from ethoxyacetyl chloride in the presence of dimethylaniline; it has an acid taste, but compares favourably with acetylsalicylic acid in its therapeutic action.

F. M. G. M.

**Condensation of Ethyl Oxalate with Ethyl Tricarballoylate.** HENRI GAULT (*Compt. rend.*, 1910, 150, 1341—1343).—In presence of sodium ethoxide, ethyl oxalate condenses with ethyl tricarballoylate to form a mixture of ethyl xalotricarballoylate and ethyl cyclopentandione-1:2:3-tricarboxylate. Wislicenus (*Abstr.*, 1896, i, 604) gives m. p. 123° for the latter compound, and states that he was unable to effect hydrolysis by acids or alkalis. The present author gives m. p. 127°, and finds that hydrolysis with hydrochloric acid leads to the formation in the first place of *ethyl cyclopentandione-1:2-dicarboxylate*,  $\text{CO}-\text{CH}(\text{CO}_2\text{H})-\text{CH}(\text{CO}_2\text{H})-\text{CH}(\text{CO}_2\text{H})-\text{CH}(\text{CO}_2\text{H})-\text{CO}$ . This substance has m. p. 137°, and develops a reddish-violet coloration with ferric chloride; it forms a *disemicarbazone* and a *diphenylhydrazone*, m. p. 190° (decomp.). Prolonged hydrolysis of the triethyl ester results in the formation of *cyclopentandione-carboxylic acid*,  $\text{HO}-\text{C}(=\text{CH})-\text{CH}(\text{CO}_2\text{H})-\text{CH}(\text{CO}_2\text{H})-\text{CO}_2\text{H}$ . This has m. p. 137°, gives a red coloration with ferric chloride, and forms a hygroscopic *disemicarbazone* and a *diphenylhydrazone* having m. p. 220° (decomp.). W. O. W.

**Action of Alcoholic Ammonia on Acetyltannin and Triacetylgallic Acid.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1910, 43, 1688—1690).—By the action of alcoholic ammonia on acetyltannin at the ordinary temperature, a mixture of products is formed; at the temperature of the water-bath, gallic acid and gallamide are obtained with other products.

Triacetylgallic acid, when treated with 3 mols. of alcoholic ammonia in the cold, forms *diacetylgallic acid*, crystallising in tiny needles, m. p. 174—176°; this gives a dark green coloration with ferric chloride, and a red coloration with potassium cyanide. It is suggested that the *p*-acetyl group is the one eliminated. E. F. A.

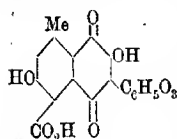
**Schiff's Digallic Acid or Artificial Tannin.** PIETRO BIGINELLI (*Ber.*, 1910, 43, 1541—1543).—A reply to Nierenstein (this vol., i, 265). The author maintains that Schiff's digallic acid contains an arsenic compound (compare Biginelli, *Abstr.*, 1909, i, 801). The reason why Nierenstein could not detect arsenic was that he did not destroy the organic matter. J. J. S.

**Dye of Kermes.** OTTO DIMROTH (*Ber.*, 1910, 43, 1387—1401).—*Kermesic acid*,  $\text{C}_{18}\text{H}_{12}\text{O}_9$ , the name given by the author to the dye isolated by a slightly modified form of Heise's process from kermes (*Coccus ilicis*), is very similar to carminic acid in tinctorial properties and in its absorption spectrum, but differs from it by its solubility in ether, a property which suggests that the molecule of kermesic acid is smaller than that of carminic acid, and contains fewer hydroxyl groups. Kermesic acid crystallises in brick-red needles, darkens at 250° without melting, and dissolves without decomposition in concentrated sulphuric acid, forming a violet-red solution, the absorption spectrum of which is very similar to that of carminic acid, and both spectra experience the same change by the addition of boric acid.

# ABSTRACTS OF CHEMICAL PAPERS

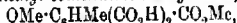
Kermesic acid is a monocarboxylic acid, which forms a tetra-acetyl derivative,  $C_{18}H_8O_8Ac_4$ , m. p. 245°, and does not contain methoxyl groups. The disodium and the barium salts are described. The red colour of a dilute alcoholic solution of the acid remains unchanged by the addition of one equivalent of potassium hydroxide, and becomes violet when two equivalents have been introduced. This acid is reduced by hydriodic acid to a red substance,  $C_{18}H_{12}O_8$ , which decomposes at 275°, and is oxidised by warm concentrated nitric acid to nitrococcussic acid, the longest known degradation product of carminic acid.

The paper deals mainly with the degradation products of kermesic acid identical with those of carminic acid; an examination of these

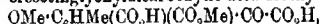


products leads the author to suggest the annexed formula for kermesic acid, similar to that of carminic acid. Several methylated derivatives can be obtained from kermesic acid. Kermesic acid trimethyl ether,  $C_{21}H_{18}O_8$ , m. p. 310°, is obtained by boiling a suspension of potassium kermesate in toluene with methyl sulphate, digesting the crystalline product

with potassium carbonate, and decomposing the insoluble portion with warm dilute hydrochloric acid; the ether is finally crystallised from glacial acetic acid, from which it separates in orange-red needles. Its oxidation by hot potassium permanganate leads to the formation of two acids. One is methyl cochenillate methyl ether,



which yields an anhydride, m. p. 149°, at its m. p., 178–180°, and is hydrolysed by 25% potassium hydroxide to cochenillic acid methyl ether,  $C_{11}H_{10}O_7$ , m. p. 200° (decomp.); both ester and acid are converted into hydroxyvutic acid by hydriodic acid, D 2·0. The other acid is a methyl ester of cresotinglyoxyldicarboxylic acid methyl ether,



m. p. 108–110° (the hydrated acid has m. p. 86°), which forms a phenylhydrazone, m. p. 183°, and is oxidised by sodium carbonate and potassium permanganate to methyl cochenillate methyl ether.

[With HAMBURGER.]—The last-mentioned compound is obtained, together with cochenillic acid methyl ether, when methyl carminate methyl ether is heated on the water-bath with nitric acid. C. S.

Influence of Ortho-substituents on the Formation of Aldehyde Diacetates. ERNST SPÄTH (*Monatsh.*, 1910, 31, 191–194. Compare Wegscheider and Späth, this vol., i, 155).—Fischer and Giehe (*Abstr.*, 1898, i, 311) have shown that ortho-substituents in an aldehyde facilitate the formation of acetals, with the single exception of *s*-trimethylbenzaldehyde. The author finds that the negative nitro-groups in 2:4:6-trinitrobenzaldehyde (Sachs and Everding, *Abstr.*, 1902, i, 377) retard the formation of a diacetate from the aldehyde, acetic anhydride, and two drops of sulphuric acid. A better yield of the diacetate,  $C_6H_2(NO_2)_3 \cdot CH(OAc)_2$ , is obtained when the mixture is kept for fifteen hours; it crystallises in needles, m. p. 117–118°.

J. J. S.

**Chemical Action of Light.** XVIII. GIACOMO L. CIAMICIAN and PAUL SILBER (Ber., 1910, 43, 1536—1541; *Atti R. Accad. Lincei*, 1910, [v], 19, i, 645—650. Compare Abstr., 1901, i, 36; 1903, i, 562).—Solutions of benzophenone in aromatic hydrocarbons undergo change when exposed to light in tubes for some months. In all cases benzopinacol is formed, and the hydrocarbon undergoes condensation. With a solution in cymene, a dicymyl, probably identical with Cannizzaro and Rossi's (*Annalen*, 1863, 121, 251), is formed. With a toluene solution the products are benzopinacol, Cannizzaro and Rossi's dibenzyl, m. p. 52°, and diphenylbenzylcarbinol (Hell and Wiegandt, Abstr., 1904, i, 490), which is formed by the addition of a molecule of toluene to one of benzophenone.

Benzophenone and ethylbenzene yield benzopinacol, the hydrocarbon,  $C_{16}H_{18}$ , m. p. 124° (Paterno and Chieffi, this vol., i, 42), and the additive product,  $C_{21}H_{20}O$ , which forms large, monoclinic crystals

$$[\alpha : b : c = 1.8207 : 1 : 0.6671; \beta = 86^{\circ}11']$$

When heated at 300° this compound is partly converted into benzophenone and ethylbenzene, but is also partly decomposed into water and a hydrocarbon,  $C_{21}H_{18}$ , m. p. 88°.

Benzophenone and *p*-xylene give benzopinacol, *pp'*-dimethyldibenzyl, and the additive compound,  $OH \cdot CPh \cdot CH_2 \cdot C_6H_4Me$ , *diphenyl-p-methylbenzylcarbinol*, m. p. 113°, b. p. 258—260°/24 mm.

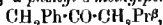
A mixture of toluene and acetone yields dibenzyl.

J. J. S.

### Ketonic Derivatives of Benzoic and Phenylacetic Acids.

JEAN B. SENDERENS (*Compt. rend.*, 1910, 150, 1336—1338. Compare Abstr., 1909, i, 286, 627; this vol., i, 11, 179, 318).—The catalytic method already described is advantageous for the preparation of the undermentioned ketones in a state of purity. The corresponding oximes and semicarbazones are best prepared by heating a solution of the ketone in 85% alcohol with pure sodium aluminate and the hydrochloride of hydroxylamine or semicarbazide. Acetophenone; propiophenone, hitherto described as a liquid, crystallises in lamellæ, m. p. 14.5°, h. p. 215°/746 mm. (corr.),  $D_4^{20}$  1.008; phenyl *n*-propyl ketone, m. p. 8.5°, b. p. 229°/746 mm. (corr.),  $D_4^{20}$  1.001; phenyl isopropyl ketone, b. p. 220°/746 mm.,  $D_4^{20}$  0.999; phenyl isobutyl ketone, b. p. 236.5°/746 mm. (corr.),  $D_4^{20}$  0.985, the oxime has m. p. 64.5°.

Dibenzyl ketone is obtained in theoretical yield by passing the vapour of phenylacetic acid over thorium oxide at 430°; the *phenylhydrazones* has m. p. 121°; the *semicarbazone*, m. p. 123°. Phenyl benzyl ketone,  $D_4^{20}$  1.019, gave a *semicarbazone*, decomposing at 165—180°;  $\alpha$ -phenylbutan- $\beta$ -one, b. p. 230°/755 mm. (corr.),  $D_4^{20}$  1.002, gave a *semicarbazone*, m. p. 135.5° (decomp.);  $\alpha$ -phenylpentan- $\beta$ -one, b. p. 244°/760 mm.,  $D_4^{20}$  0.984, the *semicarbazone* has m. p. 82°;  $\alpha$ -phenyl- $\gamma$ -methylbutan- $\beta$ -one, b. p. 237°/760 mm. (corr.),  $D_4^{20}$  0.985, the *semicarbazone* has m. p. 126°;  $\alpha$ -phenyl- $\delta$ -methylpentan- $\beta$ -one,

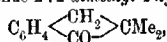


b. p. 250.5°/760 mm. (corr.),  $D_4^{20}$  0.969, gave a *semicarbazone*, m. p. 80°, and a *phenylhydrazone*, crystallising in yellow needles, m. p. 67°.

W. O. W.

**Duplobenzylidenethioacetone; a Correction.** EMIL FROMM (*Ber.*, 1910, 43, 1759. Compare Aher., 1907, 1, 710).—The so-called duplobenzylidenethioacetone is a mixture of a non-basic substance and one or more basic compounds which form salts with mineral acids. It is now found that these compounds contain about 4% of nitrogen, which explains their basic properties, and renders the explanation given formerly (*loc. cit.*) quite unnecessary. E. F. A.

**Preparation and Properties of 2:2-Dialkyl-1-hydrindones or 2:2-Dialkyl-1-indanones.** ALBIN HALLER and EDMOND BAUER (*Compt. rend.*, 1910, 150, 1472—1478. Compare Kipping, *Trans.*, 1894, 65, 480, *Proc.*, 1901, 17, 181; Haller and Bauer, *Abstr.*, 1909, i, 109, 655).—Alkylation of 1-hydrindone by means of an alkyl halide in presence of sodamide leads to the production of a dialkyl derivative identical with that obtained by Kipping's method from a substituted  $\beta$ -phenylpropionic acid; thus 2:2-dimethyl-1-hydrindone,

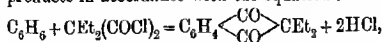


was prepared in 80% yield by warming an ethereal solution of hydrindone with sodamide in absence of air, boiling with methyl iodide for an hour, isolating the product, b. p. 116—120°/16 mm., and repeating the methylation, using benzene as the solvent. The compound was also obtained by the action of aluminium chloride on  $\beta$ -phenyl- $\alpha$ -dimethylpropionyl chloride, m. p. 5°, b. p. 125—126°/15 mm. 2:2-Dimethyl-hydrindone forms magnificent crystals, m. p. 44—45°; when heated with sodamide in benzene it yields  $\beta$ -phenyl- $\alpha$ -dimethylpropionamide. The semicarbazone forms needles, m. p. 209—210°.

2:2-Diethylhydrindone,  $\text{C}_{13}\text{H}_{16}\text{O}$ , has m. p. 7°, h. p. 138°/13 mm., and does not form a semicarbazone. The following compounds are described in connexion with its preparation.

$\beta$ -Phenyl- $\alpha$ -ethylpropionophenone,  $\text{COPh}\cdot\text{CHEt}\cdot\text{CH}_2\text{Ph}$ , arising from the action of benzyl chloride on phenyl *n*-propyl ketone in presence of sodamide, has h. p. 183—185°/14 mm., and forms an *oxime*, m. p. 70°.  $\beta$ -Phenyl- $\alpha$ -benzyl- $\alpha$ -propylpropionophenone,  $\text{COPb}\cdot\text{CPr}^n(\text{CH}_2\text{Ph})_2$ , is also formed in this reaction, and crystallises in needles, m. p. 67—68°.  $\beta$ -Phenyl- $\alpha$ -diethylpropionophenone,  $\text{COPh}\cdot\text{CET}_2\cdot\text{CH}_2\text{Ph}$ , obtained as a liquid, b. p. 190—202°/13 mm., by ethylation of  $\beta$ -phenyl- $\alpha$ -ethylpropionophenone, slowly crystallises in tablets, m. p. 80—80.5°.  $\beta$ -Phenyl- $\alpha$ -diethylpropionyl chloride has h. p. 148°/13 mm. W. O. W.

**Synthesis of the Higher Indandiones.** MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1910, 373, 291—336).—Benzene and other aromatic hydrocarbons readily condense with diethylmalonyl chloride in the presence of aluminium chloride, yielding indandiones as the chief products in accordance with the equation:

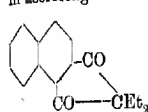


carbon disulphide usually being employed as the solvent; thus equal molecular quantities of benzene and the chloride yield a very small amount of  $\gamma$ -dibenzoylpentane,  $\text{CEt}_2(\text{COPh})_2$ , m. p. 103—104°, the chief product being 2:2-diethylindan-1:3-dione,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{CEt}_2$

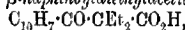
b. p. 147—156°/10 mm.,  $D_{15}^{20}$  1.062, which forms a *dioxime*, m. p. 142—144°, yields phthalic acid by oxidation with nitric acid at 130—140°, and benzoic acid by heating with concentrated potassium hydroxide. When two molecular proportions of benzene are employed in the condensation, a third product is obtained,  $\beta$ -hydroxy- $\beta\beta$ -diphenyl- $\alpha$ -diethylpropiolactone,  $\text{CET}_2\langle\text{CPh}_2\rangle\text{CO}$ , m. p. 89—90°.

Condensation with *p*-cymene yields only 4-methyl-2:2-diethyl-7-isopropylindandione,  $\text{C}_6\text{H}_3\text{MePr}\langle\text{CO}\rangle\text{CET}_2$ , m. p. 37—38.5°, the constitution of which follows from its oxidation to prehnitic acid by nitric acid at 130°.

With more complex hydrocarbons increasing difficulty is encountered in ascribing constitutions to the resulting indandiones. Naphthalene

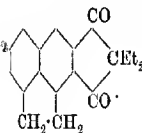


yields three isomeric products: I, a yellow *solid*, m. p. 79—81°, which receives the annexed constitution on account of its oxidation to prehnitic acid; II, a colourless *solid*, m. p. 120.5—122°, in which condensation has occurred at positions 2 and 3 of the naphthalene nucleus, since boiling concentrated aqueous potassium hydroxide decomposes the substance, forming  $\beta$ -naphthoyldiethylacetic acid,



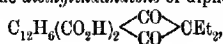
m. p. 128—12° F, which is oxidised by nitric acid at 120—140° to trimellitic acid; III, an *oil*, b. p. 210—212°/6 mm., which is very stable to alkali, and receives the only remaining possible constitution in which condensation has occurred in the *peri*-position.

The constitutions of the two indandiones obtained from acenaphthene follow very much from analogy to those of the naphthindandiones;  $\alpha$ -diethylacenaphthindandione, m. p. 153—155°, is yellow, and is converted by concentrated potassium hydroxide into  $\alpha$ -diethylacenaphthindandionic acid,  $\text{C}_{19}\text{H}_{20}\text{O}_3$ , m. p. 163—164°; it receives the annexed constitution.  $\beta$ -Diethylacenaphthindandione, m. p. 109—111°, is intensely yellow, and has the



group  $\text{CET}_2\langle\text{CO}\rangle$  in positions 1:2.

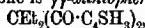
The condensation of anthracene (without carbon disulphide) yields only diethylanthraceneindandione,  $\text{C}_{21}\text{H}_{18}\text{O}_3$ , m. p. 104—105°, which is oxidised by chromic and acetic acids to the *quinone*,  $\text{C}_{21}\text{H}_{16}\text{O}_4$ , m. p. 193—194°, and is converted by concentrated potassium hydroxide into diethylanthraceneindandionic acid,  $\text{C}_{21}\text{H}_{20}\text{O}_3$ , m. p. 209—210° (decomp.). The condensation of phenanthrene yields diethylphenanthreneindandione,  $\text{C}_{22}\text{H}_{18}\text{O}_3$ , m. p. 137—139°, b. p. 254—273°/10 mm., which is converted by potassium hydroxide into diethylphenanthreneindandionic acid, m. p. 155°, and by chromic and acetic acids into the *quinone*,  $\text{C}_{21}\text{H}_{16}\text{O}_4$ , m. p. 223—224°, which is further oxidised by the acids, when hot, to the diethylindandions of diphenic acid,



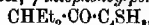


m. p. 235°. The condensation with retene yields *diethylreteneindandione*,  $C_{25}H_{24}O_2$ , m. p. 134—135°, which yields the *quinone*,  $C_{25}H_{24}O_2$ , m. p. 193—194°, by oxidation.

The condensation with thiophon yields two products, neither of which is an indandione: one is  $\gamma\gamma$ -*dithiophenoylpentane*,



m. p. 152—153°; the other,  $\gamma$ -*thiophenoylpentane*,



b. p. 146—147°/22 mm.,  $D^{20}_D$  1.058, and  $n_D$  1.53153.

Many of these indandiones and indandionic acids develop characteristic colorations with concentrated sulphuric acid; tabulated lists of these are given.

C. S.

**Constitution of  $\beta$ -Bromocarmin.** GEORG ROHDE and G. DORFMÜLLER (*Ber.*, 1910, 43, 1363—1370).— $\beta$ -Bromocarmin was considered by von Miller and Rohde (*Abstr.*, 1894, i, 94) to be a substituted bromohydroxy- $\alpha$ -naphthoquinone derivative; Liebermann and Voswinckel (*Abstr.*, 1897, i, 539; 1909, i, 487) regarded it as an indone derivative.

$\beta$ -Bromocarmin, when warmed with acetic anhydride and a drop of sulphuric acid, forms an *acetyl* derivative crystallising in yellow needles, m. p. 229°; this is no longer acid, and the composition is such that it cannot be derived from a substance of the formula proposed by Liebermann and Voswinckel.

By reduction of  $\beta$ -bromocarmin with zinc dust and acetic acid and subsequent acetylation, a compound,  $C_{17}H_{14}O_4Br_2$ , crystallising in minute, colourless needles, m. p. 208°, is obtained, which has the annexed formula, agreeing with the constitution of Miller and Rhode, but which is not in agreement with the indone structure.

Hydrolysis and oxidation by means of alkaline hydrogen peroxide yields a substance, crystallising in orange prisms, m. p. 258°, in which probably a hydroxyl group has entered the quinone nucleus (annexed formula).

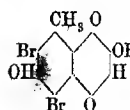
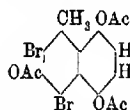
On acetylation, greenish-yellow needles, m. p. 233°, of a *diacetyl* derivative were obtained. The hydrolysis and oxidation product is only slightly attacked by bromine, small quantities of  $\alpha$ -bromocarmin being formed.

Both this product and  $\beta$ -bromocarmin yield naphthalene when distilled with zinc dust.

On reduction and subsequent acetylation of bromohydroxy- $\alpha$ -naphthoquinone a substance crystallising in colourless needles, m. p. 159°, is obtained, in which neither hydroxyl nor bromine is replaced by hydrogen. This behaviour is attributed to the negative groups in the second nucleus of bromohydroxynaphthoquinone.

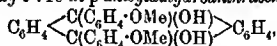
E. F. A.

**Action of Magnesium Derivatives of *o*- and *p*-Bromoanisole on Anthraquinone and  $\beta$ -Methylantraquinone.** ALEIN HALER and A. COMTESSE (*Compt. rend.*, 1910, 150, 1290—1295. Compare *Abstr.*, 1904, i, 314, 659, 660; Guyot and Staehling, *Abstr.*, 1905, i, 885; 1906, i, 17).—The organomagnesium derivatives of *o*- and



*p*-bromoanisole reacts with anthraquinone and methylanthraquinone in the same manner as the magnesium derivatives of benzene and naphthalene already studied.

9:10-Dihydroxy-9:10-di-*p*-anisylidihydroanthracene,

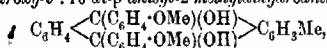


obtained from anthraquinone and magnesium *p*-anisole bromide, is a colourless, microcrystalline substance, m. p. 267°. Sulphuric acid develops a red coloration, changing to violet, then to blue, and becoming green on dilution. Dimethylaniline gives a blue coloration, changing to rose-violet. The diethyl ether has m. p. 280—281°.

9:10-Dihydroxy-9:10-di-*o*-anisylidihydroanthraquinone, occurring in microscopic crystals, m. p. 285°, forms a blue solution in sulphuric acid, changing to green, and becoming brown on heating or dilution. When boiled with zinc and glacial acetic acid it yields di-*o*-anisyl-

anthracene,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \\ \diagdown \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} \text{C}_6\text{H}_4$ , crystallising in yellow needles, m. p. 280—281°. Di-*p*-anisylanthracene forms yellow needles, m. p. 279—280°, and, like the ortho-compound, dissolves sparingly in organic solvents, giving bluish-violet solutions, which show magnificent fluorescence.

9:10-Dihydroxy-9:10-di-*p*-anisyl-2-methyldihydroanthracene,



prepared from  $\beta$ -methylanthraquinone, separates from benzene in efflorescent crystals, m. p. 208°; with sulphuric acid it develops an intense, eosin-red coloration, changing to blue, and on dilution to green. Dimethylaniline gives a green coloration, changing to brown. The isomeric di-*o*-anisyl compound forms efflorescent crystals, m. p. 260°, and gives an intense malachite-green coloration with sulphuric acid; glacial acetic acid and dimethylaniline give a brilliant-green coloration, changing to olive. Di-*p*-anisyl- $\beta$ -methylanthracene crystallises in yellow needles, m. p. 214—215°; its solutions are reddish-violet and highly fluorescent. Di-*o*-anisyl- $\beta$ -methylanthracene resembles the para-isomeride, and has m. p. 165—167°.

Attempts to convert the foregoing diols into diphenols by heating with hydrogen bromide were unsuccessful. W. O. W.

Attempts to Prepare Thiazine Dyes of the Anthraquinone Series. EDUARD LAUBÉ and J. LIEBKIND (*Ber.*, 1910, 43, 1730—1734).

—Whereas diamino-1-anilinoanthraquinone reacts readily with sulphur, forming a thiazine dye, the 2-anilino-derivative gives a variety of products, and only very little sulphur compound. Apparently, an amino-group is eliminated, and the basic properties are much lessened, so that it is doubtful whether the sulphur compounds are true thiazine dyes.

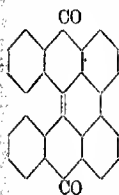
1-*op*-Dinitroanilinoanthraquinone, prepared from aminoanthraquinone and chlorodinitrobenzene in presence of copper acetate or copper powder, separates in well formed, brown, lustrous needles, m. p. 341° (corr.). The corresponding 2-*op*-dinitroanilinoanthraquinone crystallises in beautiful yellow, lustrous needles, m. p. 275° (corr.).

1-op-Diaminoanilinoanthraquinone, obtained by reducing the nitro-compound with sodium sulphide, forms small, reddish-violet crystals, m. p. above 350°, which give a reddish-violet, metallic streak on glazed porcelain. 2-op-Diaminoanilinoanthraquinone forms black needles, m. p. 255°, and makes a brownish-red streak on porcelain.

The 1-anthrathiazine,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2 \begin{smallmatrix} \diagup NH \\ \diagdown S \end{smallmatrix} C_6H_3 \cdot NH_2$ , is obtained from 1-op-diaminoanilinoanthraquinone by heating it at 150–200° with sulphur and sodium sulphide. It dyes cotton in fast green shades. The corresponding dye from the 2-anilino-compound is obtained in small quantities only, and dyes cotton in fast brown shades.

E. F. A.

Vat Dyes of the Anthracene Series. XV. *meso*Benz-dianthrone (Helianthrone), *meso*Naphthadanthrone, and a New Method of Preparing Flavanthren. ROLAND SCHOLL, JOHANNES MANSFELD [and, in part, JULIUS POTSCHWAUSCHEG] (*Ber.*, 1910, 43, 1734–1746. Compare this vol., i, 264, 272).—Copper powder in presence of concentrated sulphuric acid at the ordinary temperature



acts as a reducing agent on dianthraquinonyl, eliminating two oxygen atoms and forming a binuclear quinone, which it is proposed to name 1:9-, 1':9'-, or *mesobenz*-dianthrone (annexed formula). The compound was at first described under the name helianthrone. It contains the two chromophores in conjugated position, and, accordingly, should give only one reduction product of the anthrahydroquinone type, namely, a dihydro-compound. Only one, a green, reduction vat is formed by *mesobenz*anthrone.

When heated with anhydrous aluminium chloride for a short time at 140–145°, it is quantitatively converted into 1:9:8-, 1':9':8'-, or *mesonaphthadanthrone* (annexed formula). On nitration 1:1'-dianthraquinonyl, a mixture of dinitro-derivatives is obtained, which, when reduced with potassium sulphide, shows the presence of small quantities of flavanthren. The unknown 2:2'-dinitro-1:1'-dianthraquinonyl must have been formed and reduced to the corresponding 2:2'-diamino-derivative, which undergoes spontaneous change into flavanthren.



1:1'-Dianthraquinonyl was prepared by reduction of iodoanthraquinone in yellow or brownish-yellow crystals, m. p. 340–345°. The *tetrabromide*, produced by bromination in acetic acid in presence of iodine, forms dark needles. On nitration, in addition to the 2:2'-dinitro-derivative which was not isolated, two other isomerides in about equal quantities were obtained.  $\alpha$ -Dinitro-1:1'-dianthraquinonyl is a yellow powder, m. p. above 360°, and insoluble in boiling acetic acid. On reduction, the corresponding *diamino*-compound, a glistening, red powder, is formed.  $\beta$ -Dinitro-1:1'-dianthraquinonyl is a yellow powder, decomp. 240°, soluble in boiling acetic acid. The *diamino*-compound is a dark brownish-red powder.

1:1'-Dianthraquinonyl may be reduced to *mesobenz*dianthrone by

means of zinc dust and acetic acid at 60–70°, stannous chloride at 150°, zinc dust and fused zinc chloride at 280–290°, alcoholic potassium hydroxide at 200°, or, best of all, copper powder and concentrated sulphuric acid. *meso*Benzdianthrone dissolves in organic solvents to yellow solutions with a green fluorescence. *Tetrabromo-mesodianthrone* forms yellowish-brown needles, and yields a green reduction vat which dyes glistening, golden-yellow shades.

The green vat produced by reducing *mesobenzdianthrone* with hot alkaline sodium hyposulphite is a dihydro-derivative, since it forms *di-p-bromobenzoyldihydromesobenzdianthrone* on treatment with bromobenzoyl chloride.

*mesoNaphthodianthrone* forms brown needles from nitrobenzene; it dissolves in concentrated sulphuric acid with a red coloration and brown fluorescence. E. F. A.

**Reduction Products of *meso*Benzdianthrone (Helianthrone).** JULIUS POTTSCHWAUSCHG (*Ber.*, 1910, 43, 1746–1748).—*meso*Benzdianthrone when shaken with acetic anhydride and zinc dust at the ordinary temperature yields *diacetyldihydromesobenzdianthrone* in the form of a brown powder soluble in chloroform or acetic anhydride with an olive-green or green fluorescence, and in concentrated sulphuric acid with a green coloration which becomes violet above 200°.

Reduction of *mesobenzdianthrone* in boiling acetic anhydride yields *tetrahydromesobenzdianthrone* in the form of a black, amorphous acetyl derivative, which is hydrolysed by methyl-alcoholic potassium hydroxide. The blackish-brown, amorphous powder shows a brownish-green fluorescence in chloroform; the solution in concentrated sulphuric acid is green, and becomes brown on heating at 240–260°.

When the reduction is prolonged for thirty hours, the acetyl derivative of *hexahydromesobenzdianthrone* is obtained as a brown, amorphous powder, and hydrolysed by prolonged boiling with methyl-alcoholic potassium hydroxide. E. F. A.

**Dihydrocumyl Alcohol, Nerol, and Terpeneol in Bergamot Oil.** FRITZ ELZE (*Chem. Zeit.*, 1910, 34, 538).—In preparing "terpeneless bergamot oil," an ester fraction,  $D^{15}_D$  0.896,  $n_D^{20} = 1.0^\circ 45'$ , was obtained, which on hydrolysis yielded a mixture of alcohols,  $D^{15}_D$  0.890,  $n_D^{20} = 1.0^\circ$ . From this, dihydrocumyl alcohol and nerol were isolated by conversion into phthalic acid esters, hydrolysis of these, and fractionation of the resulting mixture under reduced pressure. The portion of the original alcoholic mixture which did not react with phthalic anhydride was identified as terpeneol by conversion into the phenylurethane. T. A. H.

**Constituents of Ethereal Oils. Eksantalic Acid,  $C_{15}H_{18}O_2$ , Eksantalal,  $C_{12}H_{16}O$ , and Derivatives.** FRIEDRICH W. SEMMLER (*Ber.*, 1910, 43, 1722–1725. Compare *Abstr.*, 1909, i, 239).—To establish the constitution of eksantalic acid the crude product obtained by the oxidation of santalol with permanganate was reduced with sodium and alcohol to *dihydroeksantalic acid*,  $C_{12}H_{20}O_2$ , b. p. 164–166°/10 mm. The methyl ester was further reduced to *dihydroeksantalol*,  $C_{12}H_{22}O$ , b. p. 140–142°,  $D^{20}_D$  0.9689,  $n_D^{20}$  1.48905.

# ABSTRACTS OF CHEMICAL PAPERS

The crude ozonide of santalol was decomposed by steam, and two products obtained, one being *eksantaloides*, m. p. 157°, and the other, separated by means of the bisulphite compound, *eksantalol*,  $C_{12}H_{18}O$ , b. p. 109—110°/10 mm.,  $D^{20}_D$  0.9845,  $n_D$  1.48519,  $\alpha_D = +13.5^\circ$  (in 100 mm. tube). Heating with acetic anhydride and sodium acetate forms enol-*eksantalol acetate*,  $C_{12}H_{17}O \cdot CO \cdot CH_3$ , b. p. 130—132°/10 mm.,  $D^{20}_D$  1.018, which on oxidation with permanganate gives *noreksantalic acid*,

$C_{11}H_{16}O_5$ ,  
b. p. 143—145°/10 mm., m. p. 93°,  $\alpha_D = -12.3^\circ$  (100 mm. tube, 50% solution). The methyl ester has b. p. 102—104°/10 mm.,  $D^{20}_D$  1.023,  $n_D$  1.47348,  $\alpha_D = -25.5^\circ$  (100 mm. tube).  
E. F. A.

Chemical Action of Light. XVII. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1910, 43, 1340—1350; *Atti R. Accad. Lincei*, 1910, [v], 19, i, 532—539).—Camphor in dilute aqueous alcoholic solution in sealed tubes was exposed to the action of light for some months. The products of the reaction were acetaldehyde and campholenaldehyde,  $C_{10}H_{16}O$ , which forms a hydroxamic acid,  $C_{10}H_{15}O_2N$ , crystallising in large, colourless, fatty, lustrous plates, m. p. 118°, and is hydrolysed by dilute sulphuric acid to campholenic acid and dihydrocampholeolactone. The third product of the action of light is a ketone,  $C_{10}H_{16}O$ , which is an oil, b. p. 203—204°, and forms a semicarbazone, crystallising in colourless, minute needles, m. p. 151—152°. On oxidation, the ketone forms a dibasic acid,  $C_{10}H_{16}O_5$ , crystallising in colourless prisms, m. p. 133—134°.

Fenchone under similar conditions gave rise to carbon monoxide in considerable quantity, and to small quantities of *fenchone hydrate*,  $C_{10}H_{18}O_2$ , crystallising in plates, m. p. 138—139°. This glycol forms a *dibenzozate*, m. p. 99°, and a *dicarbanilate*, m. p. 206° (decomp.).

Exposure to light has practically no effect on methyl isobutyl ketone, mesityl oxide, or methylheptenone, but pinacolin undergoes decomposition into butylene and acetaldehyde.  
E. F. A.

Caryophyllene. II. CARL W. HAARMANN (*Ber.*, 1910, 43, 1505—1510. Compare *Abstr.*, 1909, i, 400).—Caryophyllene glycol, m. p. 120°, which had been kept in a closed bottle for four years, was found to be largely transformed into a syrup, probably  $C_{14}H_{22}O_2$ , and a mixture of two monobasic acids,  $C_{14}H_{22}O_5$ . The one acid is identical with that already described (*loc. cit.*) as melting at 201—202°; the other is much more readily soluble in ether, crystallises from acetone, and has m. p. 152°. Both acids, when heated with 5% sulphuric acid, lose water and yield anhydro-acids,  $C_{14}H_{20}O_4$ , melting respectively at 102—103° and 106°, whereas a mixture of the two has m. p. 74—78°.

A dibasic acid,  $C_{14}H_{20}O_5$ , is formed when the acid 201—202° is oxidised with nitric acid ( $D = 1.48$ ); it forms glistening, hard crystals, m. p. 225°. When the acid, m. p. 152°, is oxidised in a similar manner, a dibasic acid,  $C_{14}H_{20}O_5$ , is obtained as slender needles, m. p. 182°. This acid is quite stable towards permanganate and mixtures of nitric and sulphuric acids.

The acids m. p. 201—202° and 152° can be obtained in the

proportions 1:8 by shaking an ethereal solution of carophyllene glycol with a few drops of concentrated sulphuric acid and oxidising the resulting oil with 5% permanganate solution.

When the glycol is oxidised with permanganate, the only acid product formed is the one with m. p. 171°. The statement that two acids, m. p. 201—202° and 162°, are formed is incorrect, as their formation in previous experiments was due to the fact that the glycol had been kept for some time and had undergone change.

J. J. S.

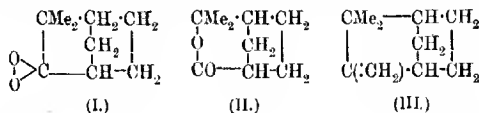
**Rotatory Power of Pinene Hydrochloride.** GUSTAVE VAVON (*Compt. rend.*, 1910, 150, 1428—1430. Compare this vol., i, 400; Ahlström and Aschan, *Abstr.*, 1906, i, 442).—A comparison has been made in the case of a number of fractions obtained by crystallisation of the hydrochlorides from French, German, and American turpentine between the rotatory power of the hydrochloride and that of the corresponding pinene and of the product of hydrogenation. The results are given in tabular form, and show that  $\alpha$ - and  $\beta$ -pinene yield equal amounts of the same hydrochloride. Similar results have been obtained from a study of the hydrobromides.

W. O. W.

**Oxidation of Camphene with Ozone.** CARL D. HARRIES and JOHN PALMÉN (*Ber.*, 1910, 43, 1432—1434. Compare Semmler, *Abstr.*, 1909, i, 170).—When an acetic acid solution of pure camphene is treated with ozone at 10°, and the solution of the ozonide then heated on the water-bath, both dimethylnorcampholide—50% (Komppa and Hintikka, *Abstr.*, 1909, i, 301)—and camphenilone are obtained.

The dimethylnorcampholide ( $\delta$ -hydroxycamphenilonolactone) and not the free hydroxy-acid is regarded as the direct product of decomposition, and its formation is attributed to the peroxide decomposition of the ozonide into peroxide (I), which is transformed readily into the isomeric lactone (II) (compare Harries and Franck, *Abstr.*, 1909, i, 132).

The formation of this lactone is in harmony with Tiemann's camphene formula (III), and the conversion of bornyl chloride into camphene involves a pinacolone transformation.



Camphenilone was isolated as its semicarbazone,  $\text{C}_{10}\text{H}_{17}\text{ON}_3$ , m. p. 222—223°.

J. J. S.

**Loango Copal.** M. WILLNER (*Arch. Pharm.*, 1910, 248, 265—276).—Loango copal, acid number 106.4—114.8 (direct), 114.8—120.4 (indirect), and saponification number 126.0—134.4 (hot), 142.8—154.0 (cold, after twenty-four hours), dissolves completely in

pyridine or quinoline. In its examination it is extracted first by ether, which dissolves 74.9%, and then with ether-alcohol, which dissolves the remainder with the exception of about 2%, consisting of inorganic matter containing sodium, potassium, calcium, magnesium, iron, and silica.

The ethereal abstract is treated successively with 0.5% ammonium carbonate, sodium carbonate, and sodium hydroxide. From the ammonium carbonate solution about 30% of crude acids have been obtained, from which the following have been isolated. *α-Loangocopallic acid*,  $C_{25}H_{48}O_2$ , m. p. 134°, a monobasic acid containing one ethylenic linking, forms a lead salt insoluble in alcohol, and has acid number 154.0—158.2 (direct), 164.9—165.8 (indirect), saponification number 177.2—177.8 (cold), 180.0—181.4 (hot), and iodine number 78.4—80.4. *β-Loangocopallic acid*,  $C_{15}H_{30}O_2$ , m. p. about 56°, a monobasic acid containing one ethylenic linking, forms a lead salt soluble in alcohol, and has acid number 192.1—194.3 (direct), 198.2—199.9 (indirect), saponification number 203.5—204.7 (hot), 199.4—201.3 (cold), and iodine number 105.3—109.4.

*Loangocopallic acid*,  $C_{18}H_{34}O_2$ , m. p. 60°, obtained from the crude acids isolated from the sodium carbonate extract, has acid number 185.1—187.3 (direct), 191.2—193.4 (indirect), saponification number 192.3—196.0 (hot), 199.1—200.2 (cold), and iodine number 88.7—88.1, and forms a lead salt which is insoluble in alcohol.

From the ether-alcohol solution, 0.5% sodium hydroxide extracts *β-loangocopal resin*,  $C_{22}H_{40}O_2$ , m. p. 200°, which is insoluble in hot alcohol, and *loangocopallic acid*,  $C_{24}H_{44}O_2$ , m. p. 165°, which is soluble in hot alcohol, and has acid number 146.2—148.7 (direct), 153.2—154.3 (indirect), saponification number 161.5—163.2 (cold), 166.7—168.9 (hot), and iodine number 70.2—71.6. C. S.

Sierra Leone Copal. M. WILLNER (*Arch. Pharm.*, 1910, 248, 285—293).—Sierra Leone copal, acid number 108.6—114.4 (direct), 121.2—126.6 (indirect), saponification number 145.9—150.1 (hot), 142.8—146.7 (cold), dissolves completely in quinoline. In its examination it is extracted first by ether, which dissolves 63.4%, then by ether-alcohol, which dissolves the remainder with the exception of about 7%, the inorganic constituents of which contain sodium, potassium, calcium, magnesium, and silica.

The ethereal extract is treated successively with 0.5% ammonium carbonate, sodium carbonate, and 1% potassium hydroxide. From the crude acids isolated from the ammonium carbonate solution, *leonscopallic acid*,  $C_{25}H_{48}O_2$ , m. p. about 142°, has been obtained as an amorphous powder; it has acid number 136.4—138.0 (direct), 142.3—144.2 (indirect), saponification number 150.6—151.5 (hot), 154.0—155.7 (cold), and iodine number 64.8—65.2, and forms a lead salt which is insoluble in alcohol. *Leonscopallic acid*,  $C_{21}H_{38}O_2$ , m. p. about 133°, obtained from the crude acids isolated from the sodium carbonate extract, has acid number 157.9—159.6 (direct), 164.4—165.2 (indirect), saponification number 171.4—173.0 (hot), 176.7—178.6 (cold), and

iodine number 167—79.6, and forms a lead salt which is insoluble in alcohol.

From the ether-alcohol solution, 0.1% sodium hydroxide extracts *leoneopalatinic acid*,  $C_{14}H_{24}O_8$ , m. p. about  $184^\circ$ , which has acid number 187.9—190.1 (direct), 194.0—195.5 (indirect), saponification number 205.5—207.5 (hot), 202.2—206.6 (cold), iodine number 110.6—111.7, and forms a lead salt soluble in alcohol, and  *$\beta$ -leoneopal resin*,  $C_{14}H_{28}O_2$ , m. p. about  $195^\circ$ , a white, amorphous powder insoluble in ether. C. S.

**Glucoside of Ecballium elaterium.** ARMAND BERG (*Bull. Soc. chim.*, 1910, [iv], 7, 385—388).—This author has stated previously (Abstr., 1898, ii, 447) that elaterin exists in fruit of the squirting cucumber for the most part, if not entirely, in the form of an amorphous, yellow glucoside,  $C_{34}H_{48}O_{12}$ , which is decomposed by a specific enzyme, elaterase, also occurring in the fruit, yielding elaterin and dextrose. Power and Moore (Trans., 1909, 95, 1985) were unable to confirm the existence of this glucoside. The author has therefore repeated his experiments, and has confirmed his previous results. When boiled with dilute sulphuric acid the glucoside is hydrolysed, yielding acetic acid, dextrose, and a resinous product, probably consisting of anhydroelateridin with some impurity. (compare Hemmelmayr, Abstr., 1906, i, 973). T. A. H.

**Action of Silver Oxide on Elaterin.** ARMAND BERG (*Compt. rend.*, 1910, 150, 981—983).—Dry silver oxide is without action on elaterin; in presence of water, however, it brings about simultaneous oxidation and hydrolysis. The chief product is an amorphous, yellow substance, *elateridoquinone*,  $C_{26}H_{30}O_7$ , which is insoluble in alkalis, and does not develop a coloration with ferric chloride. The yellow colour is discharged by hydrochloric acid. Acetic acid, together with small quantities of a phenolic compound and an acid of unknown composition, have also been recognised amongst the products of the reaction. With elateridin, silver oxide yields traces of a substance insoluble in alkalis.

These observations throw doubt on the view that elaterin is an aldehydic compound. W. O. W.

**Chlorophyll. IX. Oxidation of Chlorophyll Derivatives.** RICHARD WILLSTÄTTER and YASUHIKO ASAHINA (*Annalen*, 1910, 373, 227—238. Compare this vol., i, 126).—Phylloporphyrin, pyrroporphyrin, rhodoporphyrin, and phytyochlorin, when oxidised with lead dioxide and sulphuric acid, chromic acid, or Caro's acid, yield hæmatic acid and methylethylmaleinimide (compare Küster, Abstr., 1901, i, 58, 298; 1906, i, 337), together with smaller decomposition products, such as acetic acid and carbon dioxide. The quantities of hæmatic acid and methylethylmaleinimide formed have been carefully estimated, with the result that one mol. of a porphyrin derived from chlorophyll is found to yield 1 mol. of hæmatic acid and 2 mols. of methylethylmalein-



imide. Since hamin when oxidised probably yields only 2 mols. of hematic acid (compare Küster, *loc. cit.*; Piloty, Abstr., 1909, i, 539), and does not yield methylethylmaleinimide, it follows that at least two of the four pyrrole nuclei in hamin are different from those in the porphyrins derived from chlorophyll. W. H. G.

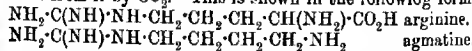
**Determination of the Constitution of the Coumaran Ketones.** CHARLES MARSHALK (*Ber.*, 1910, 43, 1695—1700. Compare Abstr., 1907, i, 950).—A direct proof of the constitution of the coumaran ketones was sought in the opening of the oxygen ring, but this does not readily take place. Coumaran, after heating with hydriodic acid, has the ring opened, forming *o*-ethylphenol, but 2-phenylcoumaran behaves altogether differently. It is now shown that benzylcoumaran, after heating with hydrogen iodide and subsequent treatment with alcoholic hydrogen chloride and zinc dust, forms *benzyl-o-ethylphenol*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{Et}\cdot\text{OH}$ , a colourless oil, b. p.  $323^\circ/718$  mm. By the action of methyl sulphate this is converted into *p-benzyl-o-ethylanisole*,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\cdot\text{Et}\cdot\text{OMe}$ , a colourless oil, b. p.  $308\text{—}312^\circ/720$  mm.,  $n=1.566$ . This constitution was established by the synthesis of the compound from *o*-ethylanisole, which was converted into the *p*-benzoyl derivative, and this reduced with sodium and alcohol to *p*-benzyl-*o*-ethylanisole. It is, therefore, established that on coupling aromatic acid chlorides with coumaran, the acid residue enters in the para-position (4) to the bridge carbon atom. E. F. A.

**Preparation of Thionaphthen Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 221465).—When compounds having the general formula  $\text{R}\langle\begin{smallmatrix} \text{S}\cdot\text{CH}=\text{CH}\cdot\text{S} \\ \text{CO}_2\text{R}_1 \quad \text{R}_1\text{O}_2\text{C} \end{smallmatrix}\rangle\text{R}$ , where R is a substituted benzene or naphthalene residue,  $\text{R}_1$  a metal, alkyl or aryl group, are heated in the presence of alkalis or alkyloxides, either with or without the addition of such reducing agents as zinc, iron or sodium hyposulphite, they yield substantive dyes of the thionaphthen series.

*3-Oxy-(1)-thiosalicyclic acid* is prepared by heating an intimate mixture of acetylene bis-*o*-thiolbenzoic acid and sodium hydroxide during half an hour at  $220\text{—}230^\circ$ , whilst the corresponding naphthalene derivative is similarly prepared from acetylene-bis-1-thiol-2-naphthoic acid.

F. M. G. M.

**Agmatine.** ALBRECHT KOSSEL (*Zeitch. physiol. Chem.*, 1910, 66, 257—251).—Agmatine,  $\text{C}_6\text{H}_{14}\text{N}_4$ , is a base which can be obtained from herring spawn after treatment with sulphuric acid at 4 atmospheres pressure in the autoclave. It was finally obtained as a crystalline aurichloride, or sulphate, and analysed. It is formed from arginine, and differs from it by  $\text{CO}_2$ . This is shown in the following formula:



W. R. H.

**Berberine.** I. Berberrubine. GUSTAV FREIBICH (*Arch. Pharm.*, 1910, 248, 276—284).—*Berberubine*,  $\text{C}_{19}\text{H}_{16}\text{O}_4\text{N}$ , m. p. about  $285^\circ$ , is obtained by heating a mixture of berberine hydrochloride and carb-

amide for half an hour at 200°, pouring the partially cooled mass into water, and extracting with chloroform; the crude base obtained by the evaporation of the chloroform is purified through the hydrochloride. The pure base separates from water in dark red leaflets and flat needles containing 3H<sub>2</sub>O; the anhydrous substance is almost black, and has an extraordinary power of absorbing water. Berberine hydroiodide is obtained by the addition of methyl iodide to berberrubine, which behaves like an internal phenoxide of the annexed constitution, assuming that the elimination of methyl alcohol from berberine occurs at the nearest methoxyl group.

The basic character of berberrubine is not great; it forms yellow, crystalline salts with strong acids, of which the *hydrochloride* and the *sulphate* are described; these are easily decomposed by alkali hydroxides or carbonates, or by ammonium hydroxide. The base is reduced to colourless *tetrahydroberberrubine*, C<sub>19</sub>H<sub>19</sub>O<sub>4</sub>N, m. p. 167–168°, by zinc in the presence of sulphuric and acetic acids.

O. S.

**The Alkaloid of *Pseudocinchona africana*.** Hydrolysis by Alkalis. ERMEST FOURNEAU (*Compt. rend.*, 1910, 150, 976–978. Compare *Abstr.*, 1909, i, 600).—The new alkaloid recently obtained from the bark of *Pseudocinchona africana* closely resembles yohimbine except in its optical rotatory power. Sodium ethoxide in alcoholic solution converts it into an acid, C<sub>20</sub>H<sub>21</sub>O<sub>3</sub>N<sub>2</sub>, isomeric with the compound obtained in the same way from yohimbine (Spiegel, *Abstr.*, 1903, i, 274). This substance crystallises from alcohol in slender, brilliant needles, m. p. below 300°, and is obtained in a hydrated form when precipitated by acids from its solutions in alkalis. The *silver* salt, C<sub>20</sub>H<sub>23</sub>O<sub>3</sub>N<sub>2</sub>Ag.H<sub>2</sub>O, is a yellow powder.

W. O. W.

**Corycavine.** C. OTTO GAEBEL (*Arch. Pharm.*, 1910, 248, 207–250).—In addition to the twelve alkaloids which have already been isolated from the rhizomes of *Corydalis cava*, the author has obtained a small amount of yet another alkaloid, C<sub>25</sub>H<sub>25</sub>O<sub>7</sub>N (?) m. p. 193–194°, [α]<sub>D</sub> 100° in chloroform, the *hydrobromide* of which decomposes at 224°.

It is noteworthy that protopine has never been isolated from *Corydalis cava*, although it is present in almost all other species of the Papaveraceae, and is regarded by Schmidt as the parent of the other Papaveraceae alkaloids.

Having at his disposal a large quantity of crude material, the author has worked up 50 grams of crude corycavine, which is finally purified by crystallisation from hot alcohol-chloroform; the mother liquor contains the new alkaloid, m. p. 193–194°.

Most of the physical and the chemical properties of corycavine recorded by previous investigators are confirmed by the author; the m. p. is given as 218–219°, and the *aurichloride*, C<sub>25</sub>H<sub>25</sub>O<sub>6</sub>N.HAuCl<sub>4</sub>, has m. p. 178–179° (decomp.). The absence of hydroxyl and of

methoxy-groups is confirmed. The presence of at least one methylenedioxy-group is proved by Weher and Tollens' process. The nitrogen is monomethylated, and is present as tervalent nitrogen in a monocyclic system, as is proved, not only quantitatively by Herzig and Meyer's method of estimating methylimino-groups, but also by the behaviour of corycavine methiodide, which, submitted to Hofmann's process of exhaustive methylation, yields successively corycavinemethine, corycavinemethine methiodide, and a non-nitrogenous, amorphous substance and trimethylamine. *Corycavinemethine*,



m. p. 153—154°, is obtained by heating corycavine methiodide with a large excess of concentrated sodium hydroxide. It separates from alcohol in white needles, develops with concentrated hydrochloric acid an intense brown, then green, and finally deep blue coloration, decolorises bromine, and yields by heating with methyl iodide, *corycavinemethine methiodide*,  $\text{C}_{22}\text{H}_{25}\text{O}_6\text{NI}$ , m. p. 218—219° (decomp.), which is converted by distillation with concentrated sodium hydroxide into trimethylamine and an amorphous substance, which does not contain nitrogen and is practically insoluble in the usual organic solvents.

Corycavine, suspended in 100 times the quantity of water, and submitted for five to six days to reduction by hydrochloric acid and zinc dust at the temperature of boiling water, yields a mixture of two bases which partly remain in the liquid and partly separate as zincchlorides. One of the bases, which is soluble in ether, is a tertiary base,  $\text{C}_{22}\text{H}_{25}\text{O}_6\text{N}$  (?), m. p. 125°, which forms well crystallised salts, contains a methylenedioxy-group, has a molecular weight of 368 by the ebullioscopic method in chloroform and also by the analysis of the *aurichloride*, and is probably formed at the expense of a methylenedioxy-group in corycavine, which therefore contains at least two such groups. The other base, the salts of which are not decomposed by ammonium hydroxide, is isolated by treating the hot aqueous solution of the zincchlorides (or the original mother liquor) with ammonium hydroxide, extracting the soluble base with ether, filtering the aqueous solution, acidifying it with acetic acid, and treating it with concentrated potassium iodide, whereby the *hydriodide* is precipitated. The *bromide*, *nitrate*, and *aurichloride*, m. p. about 185° (decomp.), are described. The pure base has not been analysed, but the intensely bitter taste of its salts, their stability to alkalis, and the formation of a new tertiary base by boiling the chloride with sodium hydroxide, indicate that the base is a quaternary ammonium hydroxide or a betaine thereof.

The oxidation of corycavinemethine in acetone at 0° by potassium permanganate yields, in addition to a small quantity of a base, m. p. 195—196°, an acid,  $\text{C}_{18}\text{H}_{15}\text{O}_7\text{N}$ , m. p. 110—111° (decomp.), which is apparently monocarboxylic. C. S.

**Papaverine and Cryptopine.** AMÉ PICTET and G. H. KRAMERS (*Ber.*, 1910, 43, 1329—1335).—Commercial papaverine shows a characteristic deep bluish-violet coloration with cold concentrated sulphuric acid, and gives more or less characteristic colorations with other alkaloid reagents. Synthetical papaverine, however, gives none of

these colorations. Commercial papaverine can be readily purified by means of the acid oxalate,  $C_{20}H_{21}O_4N, H_2C_2O_4$ , which crystallises in stellar aggregates of needles, m. p.  $196^\circ$ . The papaverine obtained from this by means of sodium hydroxide no longer gives the colour reactions which are due to admixture to the extent of 4% with another alkaloid, cryptopine (compare T. and H. Smith, *Pharm. J.*, 1867, [ii], 8, 595, 716; Hesse, this Journ., 1871, 1065).

Cryptopine crystallises in hexagonal prisms or plates, m. p.  $218^\circ$ . The dichromate forms minute, yellow prisms; the *picrate* forms long needles, grouped like a paint-brush, m. p.  $215^\circ$ ; the *mercurichloride* is colourless, m. p.  $185^\circ$ ; the *aurichloride* crystallises in brownish-yellow needles, which blacken at  $200^\circ$ , m. p.  $205^\circ$ ; the *platinichloride* forms yellow, concentrically-grouped needles, m. p.  $204^\circ$  (decomp.).

Cryptopine is a saturated base, and is not attacked by hydrogen; the stannichloride crystallises in needles, m. p.  $190^\circ$  (decomp.). It contains two methoxyl groups and one methyl attached to nitrogen.

It probably contains the methylenedioxy-group,  $CH_2 \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ , as it gives a green coloration and the characteristic absorption spectrum with sulphuric and gallic acids. It contains neither phenol nor alcoholic hydroxyl, nor a keto-group.

E. F. A.

**Compound of Acetylbromoglucose and Pyridinè.** EMIL FISCHER and CARL RASKE (*Ber.*, 1910, 43, 1750—1753).—Analogous to chlorodimethyl ether,  $\beta$ -acetylbromoglucose combines with pyridine to form *tetra-acetylglucosepyridinium bromide*. This crystallises in colourless, obliquely-cut prisms, m. p.  $174^\circ$  (corr.),  $[\alpha]_D^{20} - 6.43^\circ (\pm 0.2^\circ)$ . The crystallisation is greatly facilitated by the addition of a little phenol to the reaction mixture. The aqueous solution is neutral towards litmus, and reduces Fehling's solution only very feebly. When shaken with silver oxide, the free base is obtained, and remains as a syrup on evaporation. The only sparingly soluble salt is the *hydrogen ferrocyanide*, crystallising in stellar aggregates or bunches of needles, which are at first faintly yellowish-green, but become blue after a time or on crystallisation from hot water.

In addition to the crystalline tetra-acetylglucosepyridinium bromide, an amorphous, probably stereoisomeric, product of different rotation is obtained.

E. F. A.

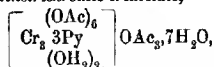
**Salts of a Hexa-acetatotripyridinetrichromi-Base.** RUNOLF F. WEINLAND and ERNST GUSSMANN (*Zeitsch. anorg. Chem.*, 1910, 67, 167—182).—When pyridine is added to a concentrated solution of hexa-acetatotrichromic diacetate (Weinland and Dinkelacker, *Ahstr.*, 1909, i, 757) and the solution is warmed, the diacetate of a new base containing 3 mols. of pyridine is obtained. The mother liquor contains a basic acetate,  $Cr_3(OAc)_3(OH)_3 \cdot 9H_2O$ , which will be described in a further communication.

The diacetate is obtained free from the accompanying pyridine acetate by precipitating with sodium acetate, and serves for the preparation of the other salts. All of these contain six acetic residues, whatever be the conditions of preparation, and these residues are therefore considered to form part of the cation complex.

m m 2

The salts with colorless acids are pale green, but concentrated solutions are dark red, becoming pale green on dilution. Some of the salts are very sparingly soluble. The secondary and tertiary salts have an acid reaction, but the primary salts are neutral. The base may be prepared by the action of silver oxide on the iodide, and forms an unstable, alkaline solution.

*Hexa-acetatotripyridinetrichromic triacetate,*



prepared by precipitating the crude acetate with sodium acetate and acetic acid, forms small, green needles, readily soluble in water. The mono- and diacetates were not completely separated. The *iodide*,

$\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ (\text{OH})_2 \end{array} \right] \text{I}$ , prepared by precipitation of the acetate solution with potassium iodide, forms almost insoluble, very pale green crystals.

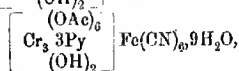
The *chloride-acetate*,  $\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ \text{OH}_2 \\ \text{OH} \end{array} \right] \text{Cl}$ ,  $\text{OAc}_3, 6\text{H}_2\text{O}$ , is precipitated by an

excess of sodium chloride. The *nitrate*,  $\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ (\text{OH})_2 \end{array} \right] \text{NO}_3, 5\text{H}_2\text{O}$ , is very sparingly soluble, one part dissolving in 216.9 parts of water.

The *nitrate-acetate*,  $\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ \text{OH}_2 \\ \text{OH} \end{array} \right] \text{NO}_3, 9\text{H}_2\text{O}$ ; the *platinichloride*,

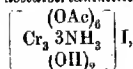
$\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ (\text{OH})_2 \end{array} \right] \frac{1}{2} \text{PtCl}_6$ ; the *stannichloride*,  $\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ \text{OH}_2 \\ \text{OH} \end{array} \right] \text{SnCl}_6, 7\text{H}_2\text{O}$ ;

the *permanganate*,  $\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3 \text{ 3Py} \\ (\text{OH})_2 \end{array} \right] \text{MnO}_4, \text{H}_2\text{O}$ ; the *ferricyanide*,



and the *chromate* have been analysed. A number of other salts are briefly described.

[With E. BÜTTNER].—Ammonia may also be introduced, by passing the gas into an alcoholic solution of hexa-acetatotrichromic diacetate. The sparingly soluble *hexa-acetatotriammine-trichromic iodide*,



resembles the pyridine compound.

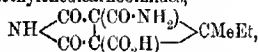
C. H. D.

Course of the Friedel-Craft Reaction with Unsymmetrical Polycarboxylic Acids. II. ALFRED KIRPAL (*Monatsh.*, 1910, 31, 295—299. Compare Abstr., 1909, i, 509).—Unlike the case of

cinchomeric anhydride (*loc. cit.*), the addition of benzene to quinolinic anhydride in the presence of aluminium chloride yields only one product, namely, 3-benzoylpicolinic acid in 92% yield. The other product, 2-benzoylnicotinic acid,  $C_6NH_5Bz \cdot CO_2H$ , m. p.  $176^\circ$ , which is not formed or only in inappreciable amount in the preceding reaction, can be prepared from benzene, 3-methyl quinolinate-2-chloride and aluminium chloride.

C. S.

**New Trimethylenepyrrole Derivatives. II.** MARIO GHIGLIENI (*Atti. R. Accad. Sci. Torino*, 1910, 45, 449—468).—The hydrolysis of the  $\alpha$ - and  $\beta$ -forms of 3:5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (compare this vol., i, 427) by 2 or more mols. of sodium hydroxide in dilute solution at the ordinary temperature consists of a reaction with  $3H_2O$ , two isomeric mono-amides of 3:5-dicarboxy-4-methyl-4-ethyltrimethylenedicarboimides,



being obtained.

The complete hydrolysis of the second cyanogen group to carboxyl is accomplished only with difficulty. It is hence evident that tertiary nitriles, which are usually regarded as hydrolysable with difficulty, can be very easily hydrolysed in certain cases. The influence of alkyl groups or neg. five radicals in hindering the hydrolysis of the cyanogen group is not general, or at any rate varies considerably according to the nature of the fundamental nucleus. The iminic group is perhaps more resistant to the action of alkali than is generally believed, and in some cases may exhibit very marked stability. Whilst the iminic hydrogen possesses a very feeble acid character when the neighbouring atoms or groups are neutral or nearly so, this character seems to be influenced regularly by the introduction of more active substituent groups, being increased by highly electronegative groups like cyanogen, and diminished to the vanishing point by the proximity of one or more acid groups.

The  $\alpha$ -amide,  $C_{10}H_{12}O_5N_2$ , prepared from  $\alpha$ -3:5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide (m. p.  $247-248^\circ$ ), forms colourless, rhombic prisms, m. p.  $194^\circ$  (decomp.) or  $232-235^\circ$  (Maquenne block). It behaves as a dihasic acid weaker than phenolphthalein; the ammonium hydrogen, sodium, and silver ( $C_{10}H_{10}O_5N_2Ag_2 \cdot 2H_2O$ ) salts were prepared.

The  $\beta$ -isomeride,  $C_{10}H_{12}O_5N_2$ , prepared from the corresponding trimethylenedicarbonimide derivative, forms shining crystals, m. p.  $206^\circ$  (decomp.), decomposes instantaneously on the Maquenne block at  $280^\circ$ . The silver salt,  $C_{10}H_{10}O_5N_2Ag_2 \cdot 2H_2O$ , was prepared.

The amide of 3-carboxy-4-methyl-4-ethyltrimethylenedicarbonimide,  $NH \begin{array}{c} \diagup CO \cdot CH \\ \diagdown CO \cdot C(CONH_2) \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} CMeEt$ , prepared by heating the  $\alpha$ -mono-amide of the dicarboxy-acid (m. p.  $194^\circ$ ) at  $165-170^\circ$ , forms shining crystals, m. p.  $141-143^\circ$  or  $142-143^\circ$  (Maquenne block), and has a feeble acidic character; its silver salt,  $C_9H_{11}O_5N_2Ag$ , was analysed.

The  $\alpha$ -dicarboxy-acid,  $NH \begin{array}{c} \diagup CO \cdot C(CO_2H) \\ \diagdown CO \cdot C(CO_2H) \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} CMeEt$ , forms small, white

needles (+ 2H<sub>2</sub>O), decomposing instantaneously on the Maquenne block at 182—183°, and is dibasic towards phenolphthalein, being the only compound of the series in which the iminic hydrogen of the pyrrole ring exhibits no acid reaction; the *sodium hydrogen* salt was analysed and various other salts prepared.

*a*-4-Methyl-4-ethyltrimethylenedicarbonimide,  $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CH} \\ \text{CO} \cdot \text{CH} \end{array} \text{CMeEt}$ ,

prepared by heating the above dicarboxy-acid, forms slender, nacreous laminae, m. p. 61—63°, and exhibits extremely feeble acid properties; when its solution is neutralised, it gives precipitates with salts of the heavy metals.

T. H. P.

**Dihydroisoindole Bases.** JULIUS VON BRAUN (*Ber.*, 1910, 43, 1353—1360. Compare Abstr., 1907, i, 960; 1909, i, 507).—A tertiary

dihydroisoindole,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{NR}$ , was sought in which the alkyl residue R, in presence of cyanogen bromide, was less firmly attached to nitrogen than the xyllyl residue of the ring. This xyllyl residue is found to take up a position between benzyl and methyl in its attachment to nitrogen; accordingly in the case of *N*-methyl- and *N*-ethyl-dihydroisoindoles the ring is opened by cyanogen bromide. *N*-Benzyl-dihydroisoindole under the same conditions has the benzyl eliminated to some extent. *N*-Allyldihydroisoindole is transformed into *N*-cyanodihydroisoindole.

*o*-Xyllylmethylaniline, prepared by the interaction of methyl-aniline and *o*-xyllyl bromide, forms a clear liquid, b. p. 200°/35 mm., m. p. 34°; the picrate has m. p. 110°. It interacts with cyanogen bromide in sealed tubes at 100°, forming a mixture of phenyl-*o*-xyllyl-cyanide, phenylmethylecyanamide, and *o*-bromo-*o*-xylene.

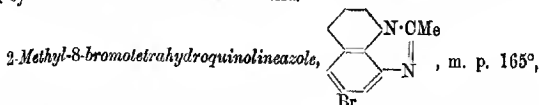
Benzylidihydroisoindole is a colourless oil, b. p. 185—186°/10 mm.; it reacts with cyanogen bromide, forming the quaternary ammonium bromide,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{N}(\text{C}_7\text{H}_7)_2\text{Br}$ , m. p. 220°. It also in part decomposes into benzyl bromide and *N*-cyanodihydroisoindole.

Allyldihydroisoindole,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{N} \cdot \text{C}_3\text{H}_5$ , prepared by the reaction of xylene bromide and allylamine in chloroform solution, has b. p. 125°/17 mm. It forms an oily *picrate* and a methiodide, m. p. 131°. It reacts very energetically with cyanogen bromide, forming allyl-bromide and *cyanodihydroisoindole*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{N} \cdot \text{CN}$ , which forms colourless crystals, m. p. 80—81°. Boiling for a short time with 25% sulphuric acid converts it into *dihydroisoindolecarboxylamide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} \text{N} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 183°. Further hydrolysis yields dihydroisoindole, b. p. 213—214°, previously prepared synthetically by Gabriel (Abstr., 1893, i, 347).

E. F. A.

**Derivatives of Tetrahydroquinoline.** II. FRANZ KUNCHELL [with W. THEOPOLD] (*Ber. deut. pharm. Ges.*, 1910, 20, 214—225).—The work described in the first part of this research (this vol., i, 429) is continued, bromomethyltetrahydroquiniminazole, dibromotetrahydroquino-

line, dibromoquinoline, and some of their derivatives being described. It has been pointed out already (*loc. cit.*) that the end product of the reduction of 6-bromo-8-nitro-1-acetyltetrahydroquinoline is a bromo-anhydro-base of the class that Bamberger and Wulz have called "quin-iminazoles" (*peri-quinolineazoles*) (Abstr., 1891, i, 1255). The reduction can be effected by tin and hydrochloric acid, as described already, or by means of zinc dust and acetic acid.



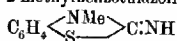
separates from light petroleum in colourless crystals, and shows none of the characteristic properties of a tetrahydroquinoline derivative. The *hydrochloride*, m. p. 253°, obtained by the action of hydrogen chloride on an ethereal solution of the base, crystallises in faintly yellow needles. The *platinichloride*, m. p. above 300°, is a brown, amorphous product.

On bromination in acetic acid, tetrahydroquinoline furnishes 5:7-dibromotetrahydroquinoline hydrobromide, m. p. 185°, which forms colourless crystals, and on addition of alkali to its solution in warm water yields the dibromo-base as a yellow, non-volatile oil. The *hydrochloride*, m. p. 178°, forms colourless crystals, and the *platinichloride*, m. p. 210° (decomp.), crystallises in small, brown needles. This dibromo-tetrahydroquinoline is probably identical with that of Hoffmann and Königs (Abstr., 1883, 1145).

5:7-Dibromo-8-nitroquinoline, m. p. 180°, prepared from 8-nitroquinoline (Knüppel, Abstr., 1896, i, 391) by heating it at 130° with water and bromine (2 mols.), crystallises from alcohol in minute, almost colourless needles. It cannot be further nitrated, and the bromine atoms are not reactive. The substance is scarcely basic, but although it forms no hydrochloride, a brown, microcrystalline *platinichloride*, m. p. 265° (decomp.), can be obtained by adding platinum chloride solution, saturated with hydrogen chloride, to a solution of the substance in alcohol, also saturated with hydrogen chloride. On heating at 230° with alcohol, saturated with ammonia at 0°, 5:7-dibromo-8-nitroquinoline is converted into the corresponding dibromoaminoquinoline, m. p. 127°, already obtained by Claus and Ammelburg (Abstr., 1894, i, 553). The *acetyl* derivative of this has m. p. 172°, and the *benzoyl* derivative, m. p. 155—156°. 5-Bromo-8-nitro-6-methylquinoline, m. p. 185—186°, prepared by heating 8-nitro-6-methylquinoline (Knüppel, Abstr., 1896, i, 391) with bromine in a closed tube at 130°, forms small, colourless crystals from a mixture of alcohol, ether, and benzene. It does not furnish a hydrochloride, but gives a *platinichloride*; the bromine atom is not attacked by aqueous or alcoholic alkali at 250°.

T. A. H.

Derivatives of Benzothiazole. EMIL BESTHORN (*Ber.*, 1910, 43, 1519—1526).—1-Imino-2-methylbenzothiazoline,



(Hugershoff, Abstr., 1903, i, 866), obtained by the action of bromine on a chloroform solution of *as*-phenylmethylthiocarbamide, is identical with



# ABSTRACTS OF CHEMICAL PAPERS.

Fischer and Besthorn's phenylmethylthiocarbazine. With nitrous acid it yields a nitroso-derivative,  $\text{C}_6\text{H}_5\text{S} \begin{smallmatrix} \text{NMe} \\ \diagup \diagdown \end{smallmatrix} \text{C:N}\cdot\text{NO}$ , which crystallises in slender, yellow needles or compact, red crystals. When gently heated, it decomposes at about  $147^\circ$ , but when heated rapidly explodes at  $152^\circ$ . It reacts with concentrated hydrochloric acid, yielding nitrous fumes, and when its xylene solution is boiled, nitrogen is evolved and 2-methylbenzothiazolone,  $\text{C}_6\text{H}_4\text{S} \begin{smallmatrix} \text{NMe} \\ \diagup \diagdown \end{smallmatrix} \text{CO}$ , is formed. This compound crystallises from ether in compact prisms, m. p.  $76^\circ$ , and yields salts with concentrated mineral acids. It is decomposed when boiled with alcoholic potassium hydroxide solution, and does not yield a phenylhydrazine.

2-Methylbenzothiazolonehydrazine,  $\text{C}_6\text{H}_4\text{S} \begin{smallmatrix} \text{NMe} \\ \diagup \diagdown \end{smallmatrix} \text{C:N}\cdot\text{NH}_2$ , obtained by reducing the nitroso-derivative with zinc dust and acetic acid at  $15^\circ$ , crystallises in colourless, thin plates, m. p.  $143\text{--}144^\circ$ , and has very feeble reducing properties at the ordinary temperature. Its hydrochloride is sparingly soluble in concentrated hydrochloric acid. The benzylidene derivative,  $\text{C}_6\text{H}_4\text{S} \begin{smallmatrix} \text{NMe} \\ \diagup \diagdown \end{smallmatrix} \text{C:N}\cdot\text{N:CHPh}$ , forms pale yellow plates, m. p.  $163^\circ$ , has but feebly basic properties, and gives a characteristic blue coloration with ferric chloride and a few drops of hydrochloric acid in aqueous alcoholic solution. J. J. S.

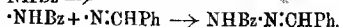
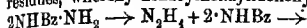
Action of Alkalis on Aromatic Acid Hydrazides. THEODOR CURTIUS and HEINRICH MELSBACH [and, in part, RISSON] (*J. pr. Chem.*, 1910, [ii], 81, 501—551).—Curtius observed (Abstr., 1900, i, 701) that the action of dilute alkali on dextrose and benzoylhydrazine in aqueous solution at the ordinary temperature produced, not benzosazones, but benzoylbenzylidene hydrazine, the dextrose apparently playing no part in the reaction. The authors have now examined the reaction fully. A known quantity (about 3 mols.) of benzoylhydrazine is dissolved in a measured volume of water, and a definite amount of sodium hydroxide (1 mol.) is added; after a definite interval of time, the precipitated benzoylbenzylidenehydrazine is collected and weighed, its purity being checked by hydrolysing it by dilute sulphuric acid, distilling the benzaldehyde with steam into a solution of hydrazine sulphate, and collecting and weighing the benzylideneazine produced.

It is found that the presence of a small quantity of dextrose increases the yield of benzoylbenzylidenehydrazine; by increasing the amount of dextrose, the yield of the hydrazide is diminished. At  $70^\circ$  the yield of benzoylbenzylidenehydrazine is considerably less than at  $40^\circ$ , or at the ordinary temperature, but again the presence of dextrose exercises a favourable influence on the yield. When the amount of sodium hydroxide is increased to 3 mols., the authors find that in experiments in which dextrose is present the product during the first four weeks is benzoylbenzylidenehydrazine, and during the next four weeks, benzylideneazine; when dextrose is not present, the only product is the azine.

The conversion of benzoylhydrazine into benzoylbenzylidenehydrazine also occurs in the presence of ammonium hydroxide, or, very slowly, in

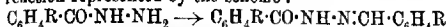
that of hydrazine hydrate. The change also takes place in alcoholic solution; in this solvent the best yield, 47·9%, of benzoylbenzylidenehydrazine is obtained; the rest of the benzoylhydrazine suffers hydrolysis, benzoic acid being produced.

The reaction is explained by the elimination of hydrazine from two molecules of benzoylhydrazine, which reduces one of the resulting residues, whereby benzoylbenzylidenehydrazine is formed:



The hydrolysis of the last by water (2 mols.) yields benzoic acid, benzaldehyde, and hydrazine, from the last two of which benzylideneazine is produced.

The reaction represented by the scheme:



has been examined in the case of other aromatic acid hydrazides. It is found that in aqueous or alcoholic solution in the presence of sodium hydroxide the conversion takes place when R is *m*-NO<sub>2</sub>, *m*-Cl, *p*-Br, *p*-Me, *o*-NH<sub>2</sub>, *o*-OH, or *p*-OMe, but not when R is *o*-NO<sub>2</sub> or *p*-NO<sub>2</sub>.

The following new compounds are described: *o*-Nitrobenzoyl-*o*-nitrobenzylidenehydrazine, NO<sub>2</sub>·C<sub>6</sub>H<sub>3</sub>·CO·NH·N·CH·C<sub>6</sub>H<sub>3</sub>·NO<sub>2</sub>, m. p. 215°; the *para*-isomeride, m. p. 274°; the *meta*-isomeride, m. p. 248°; *p*-bromobenzoyl-*p*-bromobenzylidenehydrazine, m. p. 232–233°; *p*-bromobenzylideneazine, m. p. 209·5–210°; *m*-chlorobenzoyl-*m*-chlorobenzylidenehydrazine, m. p. 147–148°; *m*-chlorobenzylideneazine, m. p. 143–144°; *o*-aminobenzoyl-*o*-aminobenzylidenehydrazine, m. p. 188–189°; *o*-hydroxybenzoyl-*o*-hydroxybenzylidenehydrazine, m. p. 277°; anisoylhydrazine, m. p. 136°; anisoylanisylidenehydrazine, m. p. 171°.

C. S.

**Relations between Constitution and Phototropy.** MAURICE PADOA and F. GRAZIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 489–495).—The relationship between constitution and phototropy observed with the tolyl- and naphthyl-hydrazones (Abstr., 1909, i, 964; this vol., i, 135) is found to hold also with the xylylhydrazones; thus, the xylylhydrazine in which Me:Me:N<sub>2</sub>H<sub>3</sub> = 1:3:4 yields non-phototropic hydrazones, whilst when Me:Me:N<sub>2</sub>H<sub>3</sub> = 1:2:4 the hydrazones are, in nearly all cases, phototropic.

*Benzaldehyde*-1:3:4-xylylhydrazone, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>N<sub>2</sub>H·CH·CHPh, forms shining, yellow scales, m. p. 86°, undergoes alteration in the air, and is not phototropic.

*Anisaldehyde*-1:3:4-xylylhydrazone, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>N<sub>2</sub>H·CH·CH·C<sub>6</sub>H<sub>4</sub>·OMe, forms slender, yellow needles, m. p. 97°, changes in the air, and does not exhibit phototropy.

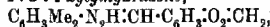
*Cinnamaldehyde*-1:3:4-xylylhydrazone, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>N<sub>2</sub>H·CH·CH·CHPh, forms lemon-yellow, non-phototropic crystals, m. p. 115°.

*Cuminaldehyde*-1:3:4-xylylhydrazone,



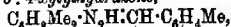
forms white needles, m. p. 76°, and is not phototropic.

*Piperonaldehyde*-1:3:4-xylylhydrazone,



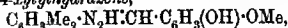
forms faintly red, non-phototropic crystals, m. p. 90°.

*p*-Tolualdehyde-1:3:4-xylylhydrazones,



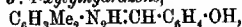
forms canary-yellow crystals, m. p. 99°, and is not phototropic.

Vanillin-1:3:4-xylylhydrazones,



crystallises in slender, yellow, non-phototropic crystals, m. p. 99°.

Salicylaldehyde-1:3:4-xylylhydrazones,



forms yellow needles, m. p. 86°, and is non-phototropic.

1:2:4-Xylylhydrazine,  $\text{NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$ , forms yellowish-white needles, m. p. 57°, and its hydrochloride, shining, white scales, m. p. 197° (decomp.).

Benzaldehyde-1:2:4-xylylhydrazones forms a faintly yellow, crystalline powder, m. p. 126°, and exhibits phototropy.

Anisaldehyde-1:2:4-xylylhydrazones crystallises in white, phototropic needles, m. p. 116°.

Cinnamaldehyde-1:2:4-xylylhydrazones forms yellow needles, m. p. 153°, and is non-phototropic.

Cuminaldehyde-1:2:4-xylylhydrazones forms slender, yellow needles, m. p. 143°, and exhibits phototropy.

Piperonaldehyde-1:2:4-xylylhydrazones crystallises as a white, phototropic powder, m. p. 118°.

*p*-Tolualdehyde-1:2:4-xylylhydrazones forms a canary-yellow, crystalline powder, m. p. 135°, and is phototropic.

Vanillin-1:2:4-xylylhydrazones forms a white, crystalline, non-phototropic powder, m. p. 118°.

Salicylaldehyde-1:2:4-xylylhydrazones forms yellowish, faintly phototropic needles, m. p. 157°.

Piperonaldehyde- $\beta$ -naphthylhydrazones (compare Rothenfusser, Abstr., 1908, i, 52) and vanillin- $\beta$ -naphthylhydrazones, m. p. 185° (Rothenfusser, *loc. cit.*, gave 187°) are phototropic.

*p*-Tolualdehyde- $\beta$ -naphthylhydrazones,  $\text{C}_{10}\text{H}_7\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in faintly yellow, phototropic scales, m. p. 188°.

Salicylaldehyde- $\beta$ -naphthylhydrazones,  $\text{C}_{10}\text{H}_7\cdot\text{N}_2\text{H}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , forms dirty-yellow needles, m. p. 187°, and is non-phototropic.

T. H. P.

Isatinanils. II. Derivatives of Thionaphthenquinone. RUDOLF PUMMERER (*Ber.*, 1910, 43, 1370—1376. Compare this vol., i, 77).—The methylene group of 3-hydroxy-1-thionaphthen reacts even more smoothly than that of indoxyl with alcoholic solutions of aromatic nitroso-compounds in the presence of sodium hydroxide, thionaphthenquinone-2-anils being formed in good yield, together with a very small amount of "thioindigo." In this way thionaphthenquinone-2-anil is obtained from nitrosobenzene; thionaphthenquinone-*p*-dimethylamino-2-anil,  $\text{C}_6\text{H}_4\cdot\text{N}(\text{CH}_3)_2$ , m. p. 176°, from *p*-nitroso-dimethylaniline; 5-methylthionaphthenquinone-*p*-dimethylamino-2-anil, m. p. 200°, from 3-hydroxy-5-methyl-1-thionaphthen; 5-chlorothionaphthenquinone-*p*-dimethylamino-2-anil, m. p. 148—149°, and 7-chlorothionaphthenquinone-*p*-dimethylamino-2-anil, m. p. 147°, from the corre-

spooding chlorinated hydroxythionaphthens; and *thionaphthenquinone-p-phenylamino-2-anil*, m. p. 193°, from *p*-nitrosodiphenylamine.

The anil group in these compounds is very loosely held. They are decomposed by mineral acids, yielding the corresponding thionaphthen-quinones, and react with substances containing a reactive methylene group, such as indoxyl, oxindole, 3-hydroxy-1-thionaphthen, or acenaphthenone, forming an indigoid dye, the anil group being eliminated as arylamine.

The salts of these anils are of interest. Isatin-*p*-dimethylamino-2-anil forms a hydrate, a yellow hydrochloride, and also an isomeric blue hydrochloride (*loc. cit.*). The latter salt may be quinonoid, but in any explanation of the isomerism a possible migration of the indole-imino hydrogen atom must not be overlooked. Such a contingency is impossible in the case of the thionaphthenquinoneanils. Thionaphthenquinone-*p*-dimethylamino-2-anil forms a yellow hydrochloride, but no hydrate, whilst thionaphthenquinone-*p*-phenylamino-2-anil forms a green hydrate, containing  $\text{H}_2\text{O}$ , and a hydrated blue hydrochloride,  $\text{C}_{20}\text{H}_{14}\text{ON}_2\text{S}, 1\frac{1}{2}\text{HCl}, 1\frac{1}{2}\text{H}_2\text{O}$ , decomposing at 120°. These facts alone do not elucidate the constitution of the blue salts, but it is noteworthy that the formation of blue salts runs *pari passu* with hydrate formation.

Thionaphthenquinone-2-oxime also is hydrolysed by boiling strong mineral acids, yielding thionaphthenquinone, and reacts with indoxyl in dilute acetic or weak mineral acid solution forming indigotin and 2-iodoxyl-2-thionaphthen-2-one.

C. S.

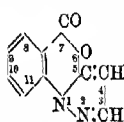
**Isatinanils. III. Leuco-compounds.** RUDOLF PUMMERER and MAXIMILIAN GÖTTLEK (*Ber.*, 1910, 43, 1376—1386. Compare preceding abstract).—*Isatin-leuco-3-anil*,  $\text{C}_{14}\text{H}_{12}\text{ON}_2$ , m. p. 192° in an atmosphere of carbon dioxide, is obtained by reducing isatin-3-anil in 2% sodium hydroxide by sodium hyposulphite and liberating the leucoanil by sodium hydrogen carbonate in an atmosphere of coal gas. It separates from benzene in colourless prisms.

*Isatin-leuco-2-anil*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{CH-NHPh}$ , m. p. 115—116°, is prepared by reducing an alcoholic solution of isatin-2-anil by a solution of sodium hyposulphite in 4% sodium hydroxide and alcohol in an atmosphere of coal gas, and decomposing the product by sodium hydrogen carbonate; it crystallises in citron-yellow prisms, and oxidises to the anil with extreme readiness. *Isatin-p-dimethylamino-leuco-2-anil*,  $\text{C}_{16}\text{H}_{17}\text{ON}_2$ , m. p. 150—155°, obtained in a similar manner is colourless, and is less readily oxidised than the preceding anil. *Isatin-leuco-2-anil* behaves in a remarkable manner with acids, concentrated sulphuric acid, dilute hydrochloric acid, hot or cold, acetic acid, or even a 1.5% boiling solution of benzoic acid, causing two simultaneous reactions, by one of which aniline and indigotin are produced, whilst the other results in the formation of aquiline, water and indirubin-2-anil. *Isatin-leuco-2-anil* is reduced extremely slowly by alkaline sodium hyposulphite, fairly rapidly to indoxyl by cold ammonium sulphide, and instantly to indigotin by warm ammonium sulphide in an atmosphere of carbon dioxide. *Isatin-2-anil*, however

is instantly reduced to indoxyl by ammonium sulphide at 0° in an atmosphere of carbon dioxide.

*Indirubin-2-anil*,  $C_6H_4 \begin{smallmatrix} \text{NH} \\ \diagup \text{CO} \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{C}_6\text{H}_5 \\ \diagdown \text{C}(\text{NPh}) \end{smallmatrix} \text{NH}$ , m. p. 219–220°, can be obtained by the interaction of isatin-leuco-2-anil and a hot alkaline solution of indoxyl (indoxylic acid), but is best prepared by slowly adding a hot alcoholic solution of isatin-2-anil to a hot aqueous-alcoholic alkaline (0.5% sodium hydroxide) solution of indoxylic acid in an atmosphere of coal gas. It separates from benzene in metallic, violet plates containing  $C_6H_6$ , forms a blue *hydrochloride*,  $C_{22}H_{15}ON_3CH$ , m. p. 245°, and yields isatin and isatin-2-anil by oxidation by potassium permanganate in glacial acetic acid. C. S.

**Anhydrides of 1-Phenyl-5 and -o-3-pyrazolonecarboxylic Acids.** AUGUST MICHAELIS (*Annalen*, 1910, 373, 129–212).—The present communication contains an account of the preparation and properties of several derivatives of a compound having the annexed constitution, which it is proposed to designate *pyrazoisocoumarazone*,



since it is formed by the union of a pyrazole ring with the *isocoumarazone* nucleus (compare Cebrian, *Abstr.*, 1898, i, 582); the anhydride of 1-phenyl-3-methyl-5-pyrazolone-2'-carboxylic acid, formed by the elimination of hydrogen chloride from 5-chloro-1-phenyl-3-methylpyrazole-2'-carboxylic acid (compare Michaelis and Eisenschmidt, *Abstr.*, 1904, i, 624), is to be regarded, therefore, as 3-methylpyrazoisocoumarazone. This compound has been isolated in three isomeric modifications; the  $\gamma$ -isomeride is formed by the distillation of 5-chloro-1-phenyl-3-methylpyrazole-2'-carboxylic acid, and passes into the  $\alpha$ -isomeride when heated with zinc chloride or water for some time, and into the  $\beta$ -isomeride when acted on by nitric or sulphuric acid or when distilled under the atmospheric pressure. 1-Phenyl-3-methyl-5-pyrazolone-2'-carboxylic acid is obtained when hydrochloric acid is added to a solution of any one of the isomerides in alkali; similarly, the same salt,  $C_{11}H_8O_2N_2 \cdot HCl \cdot H_2O$ , is formed by heating the three modifications with an excess of hydrochloric acid, yet the isomerism is not merely physical, since three isomeric 4-bromo-derivatives are formed by acting on the isomerides with bromine in glacial acetic acid.

The  $\beta$ -isomeride has also been prepared by the condensation of ethyl acetoacetate with *o*-hydrazinobenzoic acid.

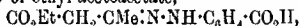
The parent substance, namely, *pyrazoisocoumarazone*, has been similarly prepared from 5-chloro-1-phenylpyrazole-2'-carboxylic acid, also the 3-phenyl derivative from 5-chloro-1:3-diphenylpyrazole-2'-carboxylic acid, and by the condensation of ethyl benzoylacetate with *o*-hydrazinobenzoic acid; isomeric forms of these compounds have not been isolated. The *pyrazoisocoumarazones* resemble *isocoumarin* and *phthalic anhydride* in their general chemical behaviour.

3-Chloro-1-phenyl-5-methylpyrazole-2'-carboxylic acid, when heated, also loses hydrogen chloride, yielding *methylbenzobispyrazolone*,  $C_6H_4 \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \diagup \text{CO} \end{smallmatrix} \text{CH}$  (compare Michaelis and Reinighaus, *Abstr.*, 1909,

i, 530), but the halogen of 4-bromo-1-phenyl-3-methylpyrazole-2'-carboxylic acid is not eliminated as hydrogen bromide by heating the acid.

[With MAX ZIESEL.]—Ethyl *o*-tolylhydrazinomethylenemalonate,  $C_6H_5Me \cdot NH \cdot NH \cdot CH : C(CO_2Et)_2$ , is prepared by the interaction of *o*-tolylhydrazine with ethyl ethoxymethylenemalonate; it forms colourless, rhombic plates and prisms, m. p.  $110^\circ$ , and is converted by aqueous sodium hydroxide into 1-*o*-tolyl-5-pyrazolone,  $C_{10}H_{10}ON_2$ , which crystallises in colourless prisms and plates, m. p.  $177^\circ$ , and when heated with phosphorus oxychloride yields 5-chloro-1-*o*-tolylpyrazole,  $C_{10}H_9N_2Cl$ , a colourless liquid with a characteristic odour; the latter substance, when oxidised with chromic acid, yields 5-chloro-1-phenylpyrazole-2'-carboxylic acid,  $C_{13}H_9O_2N_2Cl$ , which crystallises in long, colourless needles, m. p.  $125^\circ$ , and on distillation yields pyrazoisocoumarazone, colourless needles, m. p.  $116^\circ$ , b. p.  $308^\circ$ . The latter substance is converted (1) by bromine into 4-bromopyrazoisocoumarazone,  $C_{10}H_8O_2N_2Br$ , slender, colourless needles, m. p.  $199^\circ$ , and (2) by aqueous ammonia under pressure at  $120^\circ$  into 7-hydroxypyrazoquinazoline,  $OH \cdot C \begin{smallmatrix} N \\ \diagup \end{smallmatrix} \begin{smallmatrix} N \\ \diagdown \end{smallmatrix} C : CH$ , which forms small, colourless needles, m. p.  $265^\circ$ , and is converted by phosphoryl chloride into 7-chloropyrazoquinazoline,  $C_{10}H_8N_4Cl$ , pale yellow needles, m. p.  $130^\circ$ .

[With CARL KRUG, JULIUS LEO, and MAX ZIESEL.]—The *o*-carboxyphenylhydrazone of ethyl acetoacetate,

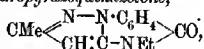


prepared by the action of *o*-hydrazinobenzoic acid on ethyl acetoacetate, forms slender, yellow needles, m. p.  $125^\circ$ , and is converted when distilled (1) under a pressure of 15 mm. into  $\beta$ -3-methylpyrazoisocoumarazone, white needles, m. p.  $132^\circ$ , and (2) under the atmospheric pressure into  $\gamma$ -3-methylpyrazoisocoumarazone, white needles, m. p.  $112^\circ$ , b. p.  $345^\circ$ ;  $\alpha$ -3-methylpyrazoisocoumarazone crystallises in white needles, m. p.  $165^\circ$ . The isomeric 3-methylpyrazoisocoumarazones, when acted on by a solution of bromine in glacial acetic acid, yield the corresponding 4-bromo-3-methylpyrazoisocoumarazones,  $C_{11}H_8O_2N_2Br$ ; the  $\alpha$ -compound forms yellow needles, m. p.  $187^\circ$ ; the  $\beta$ -isomeride crystallises in colourless needles, m. p.  $151^\circ$ ; the  $\gamma$ -modification forms colourless needles, m. p.  $135$ – $137^\circ$ , and is converted by repeated crystallisation from alcohol into the  $\beta$ -isomeride. The  $\beta$ - and  $\gamma$ -isomeric forms of 3-methylpyrazoisocoumarazone, when treated with iodine in glacial acetic acid, yield  $\gamma$ -4-iodo-3-methylpyrazoisocoumarazone,  $C_{11}H_7O_2N_2I$ , colourless, silky needles, m. p.  $182^\circ$ ; the  $\alpha$ -isomeride is not acted on by iodine in glacial acetic acid, but in the presence of iodic acid yields  $\alpha$ -4-iodo-3-methylpyrazoisocoumarazone, greenish-yellow needles, m. p.  $198^\circ$ .

3-Methylpyrazoisocoumarazone is converted by aqueous-alcoholic ammonia under pressure at  $130^\circ$  into 7-hydroxy-3-methylpyrazoquinazoline,  $C_{11}H_9ON_3$ , long, white needles, m. p.  $275$ – $276^\circ$ ; the silver salt,  $C_{11}H_8ON_3Ag$ , forms small, white needles; the chloro-derivative,  $CMe \begin{smallmatrix} N \\ \diagup \end{smallmatrix} \begin{smallmatrix} N \\ \diagdown \end{smallmatrix} C_6H_4 \\ CH : C - NCl \end{smallmatrix} CO$ , formed by the action of calcium hypochlorite

on a solution of the quinazoline in aqueous alkali, crystallises in small, red needles, m. p. 275°. 7-Hydroxy-3-methylpyrazoquinazoline is converted (1) by phosphorus trichloride into 7-chloro-3-methylpyrazoquinazoline,  $C_{11}H_8N_4Cl$ , which crystallises in glistening, yellow needles, m. p. 139°, and when treated with an alcoholic solution of sodium ethoxide yields 7-ethoxy-3-methylpyrazoquinazoline,  $C_{18}H_{18}ON_4$ , glistening, white, felted needles, m. p. 125°, and (2) by phosphorus pentachloride into 4:7-dichloro-3-methylpyrazoquinazoline,  $C_{11}H_6N_4Cl_2$ , crystallising in glistening, yellow needles, m. p. 174–175°.

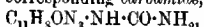
3-Methyl-6-ethylidihydropyrazoquinazoline,



is prepared by the action of ethylamine on methylpyrazoisoumarazone; it forms glistening, pale yellow needles, m. p. 133–134°; the corresponding 6-phenyl compound,  $C_{17}H_{13}ON_4$ , similarly prepared by using aniline, crystallises in colourless needles, m. p. 156°; the corresponding 6-anilino-compound,  $C_{17}H_{11}ON_4$ , obtained by using phenylhydrazine, forms lemon-yellow leaflets, m. p. 195°; the

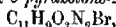
corresponding 6-amino-compound,  $CMe \begin{array}{c} \diagup N-N \cdot C_6H_4 \diagdown \\ \diagdown CH \cdot C-N(NH_2) \diagup \end{array} CO$ , pre-

pared by heating methylpyrazoisoumarazone with hydrazine hydrate at 180°, crystallises in colourless needles, m. p. 249°, and condenses with benzaldehyde and benzophenone, yielding the benzylidene derivative,  $C_{11}H_8ON_4 \cdot N \cdot CHPh$ , white needles, m. p. 174°, and diphenylmethylene derivative,  $C_{11}H_8ON_4 \cdot N \cdot CPh_2$ , white needles, m. p. 257° respectively; the corresponding carbamide,



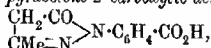
prepared by the action of semicarbazide on methylpyrazoisoumarazone, crystallises in needles, m. p. 265°.

4-Bromo-1-phenyl-3-methyl-5-pyrazolone-2'-carboxylic acid,



is formed by the action of aqueous sodium hydroxide on either of the 4-bromo-3-methylpyrazoisoumarazones; it forms colourless needles, m. p. 202°.

1-Phenyl-3-methyl-5-pyrazolone-2'-carboxylic acid,



similarly prepared from the methylpyrazoisoumarazones, forms slightly yellow crystals, m. p. 195°; the 4-oximino-derivative,



crystallises with  $1H_2O$  in rosettes of yellow needles, m. p. 139°; the anhydrous substance has m. p. 200°; the 4-benzylidene derivative,  $C_{18}H_{14}O_3N_2$ , forms white crystals, m. p. 243°; the 4-benzeneazoderivative,  $C_{17}H_{11}O_3N_4$ , crystallises in golden-yellow needles, m. p. 206°.

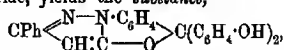
[With JULIUS LEN.]—The following compounds are prepared by methods similar to those employed in the preparation of the corresponding compounds just described: 1-o-tolyl-3:4-dimethyl-5-pyrazolone,  $C_{13}H_{14}ON_2$ , forms white needles, m. p. 179°; 5-chloro-1-o-tolyl-3:4-dimethylpyrazole,  $C_{12}H_{13}N_2Cl$ , is a white, crystalline mass, m. p. 48°;

the *methiodide*,  $C_{10}H_{11}N_2Cl.MeI$ , forms white, silky, felted needles, m. p.  $187^\circ$ ; 5-chloro-1-phenyl-3-methylpyrazole-4:2'-dicarboxylic acid,  $C_{12}H_9O_4N_2Cl$ , crystallises in slender, white needles, m. p.  $226^\circ$  (decomp.); the latter substance yields 3-methylpyrazoisocoumarazone when distilled under a pressure of 16 mm. at  $201^\circ$ , and 3-methylpyrazoisocoumarazone-4-carboxylic acid,  $C_{12}H_9O_4N_2$ , slightly yellow, slender needles, m. p.  $224^\circ$  (decomp.), when heated at  $171^\circ$  under a pressure of 16 mm.; 3-phenyl-1-o-tolyl-5-pyrazolone,  $C_{16}H_{14}ON_2$ , crystallises in glistening, white leaflets, m. p.  $191^\circ$ ; 5-chloro-3-phenyl-1-o-tolylpyrazole,  $C_{16}H_{13}N_2Cl$ , is a white, crystalline mass, m. p.  $46^\circ$ ; 5-chloro-1:3-diphenylpyrazole-2'-carboxylic acid,  $C_{16}H_{11}O_2N_2Cl$ , crystallises with  $1H_2O$  in stout, white prisms, m. p.  $239^\circ$  (decomp.); ethyl benzoylacetate o-carboxyphenylhydrazone,  $CO_2Et \cdot CH_2 \cdot CPh \cdot N \cdot NH \cdot C_6H_4 \cdot CO_2H$ , forms slender, yellow needles, m. p.  $166-167^\circ$ ; 3-phenylpyrazoisocoumarazone,  $C_{16}H_{10}O_2N_2$ , crystallises in glistening, slender, white needles, m. p.  $199^\circ$ ; 4-bromo-3-phenylpyrazoisocoumarazone,  $C_{16}H_9O_2N_2Br$ , forms glistening, white needles, m. p.  $187^\circ$ ; the corresponding 4-chloro-compound crystallises in slender, white needles, m. p.  $170^\circ$ ; 7-hydroxy-3-phenylpyrazoquinazoline,  $C_{16}H_{11}ON_3$ , crystallises in felted, white needles, m. p.  $315^\circ$ ; the crystalline potassium and silver salts were analysed; 4:6-dichloro-3-phenyldihydropyrazoquinazoline,  $C_{16}H_9ON_3Cl$ , forms slender, silky, yellow needles, m. p.  $243-248^\circ$ ; 7-chloro-3-phenylpyrazoquinazoline,  $C_{16}H_{10}N_3Cl$ , crystallises in glistening, slightly yellow needles, m. p.  $145^\circ$ ; 4:7-dichloro-3-phenylpyrazoquinazoline,  $C_{16}H_9N_3Cl_2$ , forms yellow needles, m. p.  $160^\circ$ ; 7-amino-3-phenylpyrazoquinazoline,  $C_{16}H_{11}N_4$ , forms white, silky needles, m. p.  $215^\circ$ ; 7-ethoxy-3-phenylpyrazoquinazoline,  $C_{18}H_{15}ON_3$ , crystallises in glistening, white needles, m. p.  $136^\circ$ ; 3-phenyl-6-ethyldihydropyrazoquinazoline,  $C_{18}H_{16}ON_3$ , forms glistening, white needles, m. p.  $171^\circ$ ; the corresponding 6-phenyl compound,  $C_{22}H_{18}ON_3$ , crystallises in pale yellow prisms, m. p.  $211^\circ$ ; the corresponding 6-anilino compound,  $C_{25}H_{18}ON_3$ , forms glistening, yellow leaflets, m. p.  $248^\circ$ ; the analogous 6-amino-compound,  $C_{16}H_{12}ON_3$ , forms glistening, white leaflets, m. p.  $232^\circ$  (decomp.), the benzylidene derivative of which crystallises in slender, white needles, m. p.  $185^\circ$ ; the 6-carbamide,  $C_{17}H_{13}O_2N_3$ , forms felted, white needles, m. p.  $325^\circ$  (decomp.); the 6-oximino-compound,  $C_{16}H_{11}O_2N_3$ , forms glistening, white needles, m. p.  $247^\circ$ ; 1:3-diphenyl-5-pyrazolone-2'-carboxylic acid,  $\begin{matrix} CH_2 \cdot CO \\ CPh = N \end{matrix} > N \cdot C_6H_4 \cdot CO_2H$ , crystallises in white, glistening leaflets, sinters at  $189^\circ$ , m. p.  $197^\circ$  (decomp.), and yields a barium salt ( $3H_2O$ ), felted, white needles, ethyl ester,  $C_{16}H_{11}O_2N_2 \cdot OEt$ , glistening, white needles, m. p.  $133^\circ$ , and dichloro-derivative,  $\begin{matrix} CHCl \cdot CCl(OH) \\ CPh = N \end{matrix} > N \cdot C_6H_4 \cdot CO_2H$ , slender, white needles, m. p.  $208^\circ$  (decomp.); 1:3-diphenyl-4-benzylidene-5-pyrazolone-2'-carboxylic acid,  $C_{22}H_{16}O_3N_2$ , forms glistening, white crystals, m. p.  $241^\circ$ ; the corresponding 4-oximino-compound,  $C_{16}H_{11}O_4N_2$ , crystallises in stout, scarlet needles, m. p.  $213^\circ$ ; the



corresponding 4-nitro-compound,  $C_{16}H_{11}O_3N_3$ , forms glistening, yellow leaflets, m. p.  $268^\circ$  (decomp.); the 4-benzeneazo-compound,  $C_{22}H_{16}O_3N_3$ , forms compact, glistening, bright red crystals, m. p.  $225^\circ$ ; the 4-p-tolueneazo-compound,  $C_{23}H_{18}O_3N_3$ , crystallises in glistening, orange-red needles, m. p.  $194^\circ$ .

3-Phenylpyrazoisocoumarazone, when heated with phenol and aluminium chloride, yields the substance,



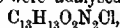
an amorphous, yellowish-brown powder, m. p.  $120^\circ$ , solutions of which in aqueous alkalis are intensely red; an analogous substance,



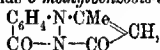
is similarly obtained by condensation with dimethylaniline; it forms glistening, white leaflets, m. p.  $216^\circ$ ; an intensely green substance is formed simultaneously.

3-Methylpyrazoisocoumarazone, when heated with resorcinol and zinc chloride, yields a substance,  $\text{C}_{19}\text{H}_{14}\text{O}_3 \cdot 2\text{H}_2\text{O}$ , which crystallises in colourless, glistening needles, m. p.  $186\text{--}187^\circ$ , and dissolves in alkalis, forming solutions with an intense blue fluorescence; 3-phenylpyrazoisocoumarazone, when similarly treated, yields a substance,  $\text{C}_{19}\text{H}_{13}\text{O}_4$ , pale yellow, rectangular plates, m. p.  $248^\circ$ , solutions of which in alkali exhibit a yellowish-green fluorescence.

[With CHRISTOPH KÄDING.]—3-Chloro-1-phenyl-5-methylpyrazole-2-carboxylic acid,  $\text{C}_{11}\text{H}_9\text{O}_2\text{N}_2\text{Cl}$ , is prepared by the oxidation of 3-chloro-1-o-tolyl-5-methylpyrazole with chromic acid; it crystallises with  $\text{H}_2\text{O}$  in white prisms, m. p.  $79^\circ$ ; the anhydrous substance has m. p.  $111^\circ$ ; the barium and silver salts were analysed; the ethyl ester,



is a colourless oil, b. p.  $325^\circ$ . The acid when heated at  $190^\circ$  under a pressure of 16 mm. yields 5-methylbezobis-3-pyrazolone,



crystallising in glistening, yellow leaflets, m. p.  $265^\circ$ , solutions of which in acetic acid, alcohol, and chloroform have a bluish-green or blue fluorescence; the 4-bromo-derivative,  $\text{C}_{11}\text{H}_7\text{O}_2\text{N}_2\text{Br}$ , forms yellow, matted needles, m. p.  $233^\circ$ , solutions of which in organic solvents exhibit a blue fluorescence. 1-Phenyl-5-methyl-3-pyrazolone-2-carboxylic acid,  $\text{C}_{11}\text{H}_{10}\text{O}_3\text{N}_2$ , is formed by dissolving 5-methylbezobis-3-pyrazolone in aqueous alkali; it crystallises in white leaflets, m. p.  $221^\circ$ ; the ammonium salt forms white prisms, m. p.  $260^\circ$ ; the ethyl ester crystallises in white, slender prisms, m. p.  $160^\circ$ ; this amide,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_3$ , is formed by heating 5-methylbezobis-3-pyrazolons with aqueous ammonia under pressure at  $210^\circ$ ; it forms white crystals, m. p.  $249^\circ$ ; the anilide,  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}_3$ , white crystals, m. p.  $161^\circ$ , phenylhydrazide,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_4$ , white leaflets, m. p.  $218^\circ$ , and hydrazide,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}_4$ , colourless crystals, m. p.  $253^\circ$ , are similarly prepared; the 4-benzeneazo-derivative,  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_4$ , forms yellowish-brown leaflets, m. p.  $210^\circ$ .

4-Bromo-1-o-tolyl-3-methylpyrazole,  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{Br}$ , is prepared by brominating 1-o-tolyl-3-methylpyrazole; it is a colourless liquid with

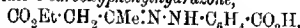
a pleasant odour, b. p.  $171^{\circ}/25$  mm., and when oxidised yields 4-bromo-1-phenyl-3-methylpyrazole-3'-carboxylic acid,  $C_{11}H_9O_2N_2Br$ , which crystallises in white prisms, m. p.  $194^{\circ}$ ; the silver salt forms white needles; the ethyl ester is a colourless oil with a pleasant odour, b. p.  $334^{\circ}$ . W. H. G.

1-Phenyl-3-methyl-5-pyrazolone-3' and 4'-carboxylic Acids.

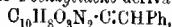
AUGUST MICHAELIS and HANS HORN (*Annalen*, 1910, 373, 213—218).

The 3' and 4'-carboxylic acids of 1-phenyl-3-methyl-5-pyrazolone have the same chemical properties as the 2'-isomeride (compare this vol., i, 514), but the chloropyrazolecarboxylic acids derived from them, when heated, do not decompose with the elimination of hydrogen chloride.

Ethyl acetoacetate-4-carboxyphenylhydrazone,

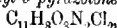


is prepared from ethyl acetoacetate and 4-hydrazinobenzoic acid; it forms slightly yellow needles, and when heated at  $150^{\circ}$  yields 1-phenyl-3-methyl-5-pyrazolone-4'-carboxylic acid,  $C_{11}H_9O_3N_2$ , pale yellow needles, m. p.  $281^{\circ}$ ; the latter substance is converted (1) by benzaldehyde into the 4-benzylidene derivative,



dark red needles, m. p.  $266^{\circ}$ ; (2) by sodium nitrite and acetic acid into the 4-oximino-derivative,  $C_{10}H_8O_3N_2 \cdot C \cdot N \cdot OH$ , yellow needles, decomposing at  $253^{\circ}$ ; (3) by diazobenzene chloride into the 4-benzene-azo-derivative,  $C_{10}H_8O_3N_2 \cdot C \cdot N_2Ph$ , slender, yellow needles, m. p.  $277^{\circ}$ ; and (4) by phosphoryl chloride into 5-chloro-1-phenyl-3-methylpyrazole 4'-carboxylic acid (compare Michaelis and Sudendorf, *Abstr.*, 1900, i, 696).

The following compounds are similarly prepared: 1-phenyl-3-methyl-5-pyrazolone-3'-carboxylic acid forms slender, white needles, m. p.  $217^{\circ}$ ; the methyl ester forms white crystals, m. p.  $86^{\circ}$ ; the ethyl ester is a pale yellow oil, b. p.  $241^{\circ}/25$  mm.; the 4-benzylidene derivative crystallises in red leaflets, m. p.  $251^{\circ}$ ; the 4-oximino-derivative forms orange-red needles, m. p.  $242^{\circ}$ ; the 4-benzeneazo-derivative forms orange-yellow leaflets, m. p.  $245^{\circ}$ ; 5-chloro-1-phenyl-3-methylpyrazole-3'-carboxylic acid crystallises in small needles, m. p.  $165^{\circ}$ . 1-Phenyl-3-methyl-5-pyrazolone-3'-carboxylic acid (1 mol.) is converted by phosphorus pentachloride (2 mols.) under pressure at  $136^{\circ}$ , and subsequent treatment with water into 4:4-dichloro-1-phenyl-3-methyl-5-pyrazolone-3'-carboxylic acid,



white needles, m. p.  $116^{\circ}$ .

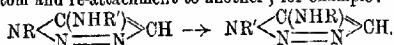
W. H. G.

Blue Reduction Product from Flavanthren. JULIUS POTSCHWAUSCHEG (*Ber.*, 1910, 43, 1748—1750).—Flavanthren, when reduced with alkaline sodium hyposulphite in an atmosphere of hydrogen, yields a mixture of products from which Scholl and Holdermann (*Abstr.*, 1908, i, 696) by means of benzoyl chloride isolated 0-benzoyldihydroflavanthren, an amorphous, reddish-brown powder.

Using *p*-bromobenzoyl chloride, a *nono-p*-bromobenzoyldihydroflavanthren is obtained, crystallising from nitrobenzene in yellow needles, which are not melted at  $360^{\circ}$ . This is insoluble in sodium

hydroxide; accordingly, the acyl residue is attached to oxygen. It dissolves in concentrated sulphuric acid with a green coloration, turning reddish-brown on heating. E. F. A.

**Intramolecular Transformations. IV. Hydroxytriazoles and Diazoamides.** OTTO DIMROTH [and, in part, HANS AICKELIN, B. BRAHN, GUSTAV FESTER, and ELSA MERCKLE] (*Annalen*, 1910, 373, 336—370. Compare Abstr., 1905, i, 98, 384; 1909, i, 267).—It has been shown previously that many 5-hydroxy-1:2:3-triazole derivatives are converted by fusion or by solution in organic solvents into neutral isomerides which have been regarded as triazolones, the change being one of enol-keto-desmotropy. Doubts of the correctness arose later when it was found that 5-aminotriazoles under the same conditions also underwent changes by detachment of the azo-group from one nitrogen atom and re-attachment to another; for example:



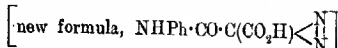
Assuming that the same change occurs in hydroxytriazoles, the neutral isomeride would be a substituted amino-derivative of a diazo-anhydride:  $NR \begin{array}{c} \text{C(OH)} \\ \text{N} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{CH} \rightarrow O \begin{array}{c} \text{C(NHR)} \\ \text{N} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{CH}$ . This explanation of the change of the hydroxytriazoles has been considered previously and rejected, because the properties of the neutral isomerides are not at all comparable with those of other diazo-anhydrides, the cyclic oxygen atom of which is very reactive (Wolff, Abstr., 1903, i, 203). Piloty and Neresheimer (Abstr., 1906, i, 146) have shown, however, that ethyl diazomalonate exhibits remarkable stability to acids and to iodine, and therefore formulate it as a diazo-anhydride,

$\begin{array}{c} \text{C(CO}_2\text{Et):C(OEt)} \\ \text{N} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{O}$ . The oxygen atom is non-reactive, showing no tendency to be replaced by sulphur or amino-groups. The stability of ethyl diazomalonate is not remarkable when it is borne in mind how the reactivity of diazomethane is diminished by the introduction of one carboxy-group. Consequently, ethyl diazomalonate may be represented by the preceding formula or by the only alternative,  $\begin{array}{c} \text{N} \\ \text{N} \end{array} \begin{array}{c} \text{C(CO}_2\text{Et)} \\ \text{N} \end{array}$ . The latter is accepted for the following reasons:

Ethyl diazomalonate is converted by cold ammonium hydroxide into ethyl diazomalonamate,  $\text{NH}_2 \cdot \text{CO} \cdot \text{CN}_2 \cdot \text{CO}_2\text{Et}$ , m. p. 143°, which is changed by sodium ethoxide into ethyl 5-hydroxy-1:2:3-triazole-4-carboxylate,  $\begin{array}{c} \text{C(CO}_2\text{Et):C(OH)} \\ \text{N} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{NH}$ , m. p. 130°; the latter is reconverted into the former by fusion. If ethyl diazomalonate has the constitution ascribed to it by Piloty and Neresheimer, the substance produced by the action of ammonium hydroxide would be either  $\begin{array}{c} \text{C(CO}_2\text{Et):C(NH}_2) \\ \text{N} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{O}$  or  $\begin{array}{c} \text{C(CO} \cdot \text{NH}_2) \\ \text{N} \end{array} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{O}$ , neither of which is satisfactory, since the substance does not contain a primary amino group, and yields a hydroxytriazolecarboxylic ester (not an amide) by treatment with sodium ethoxide.

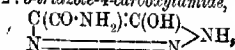
In the preceding, the author arrives at the conclusion that all the

neutral isomerides, obtained by the fusion or solution of 5-hydroxytriazoles and previously described as triazolones, possess a diazo-structure similar to that of ethyl diazomalonate, and are derivatives of diazomethane. This theory harmonises with the fact that the hydroxytriazoles are colourless, whilst their neutral isomerides are yellow, and explains such phenomena as the conversion of 5-hydroxy-1-phenyl-1:2:3-triazole-4-carboxylic acid into carbon dioxide and the corresponding hydroxytriazole by warm water, and the conversion of the neutral isomeride

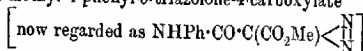


by the same means into nitrogen and glycollocanilide. The theory is supported by the two following facts. Aminomalonamide hydrochloride in aqueous solution, sodium nitrite, and a few drops of dilute

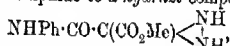
sulphuric acid at 0° yields diazomalonamide,  $\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > \text{C}(\text{CO} \cdot \text{NH}_2)_2$ , m. p. 175°, which forms yellow crystals, and is converted by sodium ethoxide into 5-hydroxy-1:2:3-triazole-4-carboxylamide,



m. p. 196°, which is colourless and reconvertible into diazomalonamide by prolonged boiling with alcohol. (The hydroxytriazole-amide is more conveniently prepared by acidifying the product obtained by the interaction of malonamide, phenylazoimide, and alcoholic sodium ethoxide.) The other fact is the reduction of the substance formerly described as methyl 1-phenyl-5-triazolone-4-carboxylate

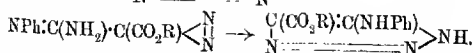


by alcoholic hydrogen sulphide to a hydrazine-compound,



m. p. 130–131°, which is colourless, does not decolorise iodine, yields hydrazine by treatment with boiling 10% hydrochloric acid, and is reconverted into the original substance by mercuric oxide; this behaviour is quite similar to that of the reduction product of ethyl diazomalonate.

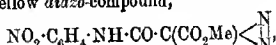
The analogy between the desmotropic change of 5-hydroxytriazoles and of 5-aminotriazoles, which apparently disappears in the new explanation of the former change, reappears with the assumption of the formation of a fugitive intermediate compound in the case of the aminotriazoles; thus,  $\begin{smallmatrix} \text{C}(\text{CO}_2\text{R}) : \text{C}(\text{NH}_2) \\ \text{N} = \text{N} = \text{N} > \text{NPh} \rightarrow \end{smallmatrix}$



It appears, therefore, that there is an intimate connexion between hydroxytriazoles of the type  $\begin{smallmatrix} \text{CR} : \text{C}(\text{OH}) \\ \text{N} = \text{N} = \text{N} > \text{NR} \end{smallmatrix}$  and diazoamides,

$\text{NHR} \cdot \text{CO} \cdot \text{CR} < \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$ . The latter are converted quantitatively and universally into salts of the former by alkaline reagents. The

converse change, hydroxytriazole  $\rightarrow$  diazoamide, by fusion or solution in organic solvents is not general, and depends on the nature of R and R'. 5-Hydroxytriazole, 5-hydroxy-1-phenyltriazole, 5-hydroxy-1-phenyl-4-methyltriazole, and 5-hydroxy-1:4-diphenyltriazole cannot be changed into the isomeric diazoamides. The presence of  $\text{CO}_2\text{R}$  or of  $\text{CO}\cdot\text{NH}_2$  in position 4 facilitates the change into the diazo-compound, which is also favoured by the presence of phenyl and especially of negatively-substituted phenyl groups in position 1; thus methyl 5-hydroxy-1-*o*-*p*-dinitrophenyl-1:2:3-triazole-4-carboxylate has so great a tendency to change that it is only stable in the form of its salts. Also, when *p*-nitrophenylazoimide and methyl sodiomalonate react in methyl alcohol, and the product is acidified and recrystallised from acetic acid, the yellow diazo-compound,



m. p.  $175^\circ$ , is obtained, the expected colourless hydroxytriazole,  $\text{C}(\text{CO}_2\text{Me})\cdot\text{C}(\text{OH})\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , only being produced by treating the yellow isomeride with sodium methoxide.

The stabilising influence of a positive radicle in position 1 is shown in the case of methyl 5-hydroxy-1-benzyl-1:2:3-triazole-4-carboxylate, m. p.  $119^\circ$ , which is obtained from benzylazoimide, methyl malonate, and methyl alcoholic sodium methoxide, and subsequent acidification of the product; it is colourless, and can be recrystallised from organic solvents without change, although by fusion it is converted into the yellow diazo-compound,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Me})\text{N}=\text{N}$ , m. p.  $45^\circ$ .

Methods of measuring the velocities of the opposed reactions, hydroxytriazole  $\rightleftharpoons$  diazo-compound, are described, and the values are tabulated and discussed. C. S.

Urazoles. XVI. Salts of Tautomeric Compounds. Reactions of Urazole Salts with Alkyl Halides. ROGER F. BRUNEL and SALOMON F. ACREE (*Amer. Chem. J.*, 1910, 43, 505—553. Compare Abstr., 1908, i, 919).—An account is given of a study of the alkylation of potassium phenylurazole by various alkyl iodides. The chief product of these reactions is the *N*-ester of the urazole, and, in most cases, evidence was obtained of the presence of some *O*-ester. In the case of the isobutyl and isamyl compounds, only traces of *O*-derivatives could be detected, whilst in other cases the amount appeared to be 10—20% of the total product.

The application of the results of these experiments to the general question of tautomerism is discussed. It is shown that the assumption of different structures for the potassium and silver salts of a tautomeric compound does not afford an explanation of the urazole reactions, since both salts yield a mixture of *O*- and *N*-esters. The theory that when a salt gives two isomeric derivatives on alkylation, one is an intermediate product in the formation of the other, does not hold in the present case, because neither derivative undergoes rearrangement into the other, and the ratio of the two products is almost the same at all

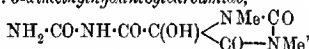
stages of the reaction. The addition theory is not valid in the case of the urazoles, since in many reactions the velocity decreases on the addition of electrolytes, whereas, according to this theory, it should increase. The results can all be explained, however, by assuming the existence of two tautomeric salts in instantaneous equilibrium.

The following compounds have been obtained: 1-phenyl-2-ethylurazole, m. p. 119°; 1-phenyl-2-n-propylurazole, m. p. 128°; 1-phenyl-2-n-butylurazole, m. p. 130°; 1-phenyl-2-isopropylurazole, m. p. 161.5°; 1-phenyl-2-isobutylurazole, m. p. 152.5°; 1-phenyl-2-isoamylurazole, m. p. m. p. 97—98°. The silver salts of all these compounds, except the last, have been prepared. 1-Phenyl-4-n-propylurazole has m. p. 120°; 1-phenyl-4-n-butylurazole, m. p. 149—150°, and 1-phenyl-4-methyl-2-ethylurazole, m. p. 52—53°.

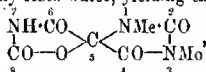
In carrying out the quantitative investigation of the reaction of the alkyl halides with urazole salts, it was necessary to maintain sealed tubes at a particular temperature for a considerable time. For this purpose a special constant-temperature water-bath was devised, which is regulated automatically and can be kept at any temperature up to 100° with a variation of not more than 0.1—0.2°. This apparatus is described.

E. G.

**Degradation of 7:9-Dimethyluric Acid.** HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1910, 43, 1589—1600).—When 7:9-dimethyluric acid 4:5-diglycol (Fischer's oxy-7:9-dimethyluric acid: compare this vol., i, 526) is heated with water or with glacial acetic acid on the water-bath for several hours, it is transformed into an isomeric, which is represented as 5-hydroxy-1:3-dimethylhydantoin-5-carbureide or 5-hydroxy-1:3-dimethylhydantoincarbamide,



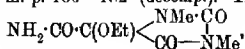
which crystallises from a mixture of ether and alcohol. It has m. p. 208° (decomp.), and when decomposed with sodium hydroxide solution at the ordinary temperature is transformed into the corresponding acid, which immediately loses water, yielding the lactone,



which is closely related to certain degradation products of caffeine, and is therefore termed 1:3-dimethylcaffolide. It crystallises from chloroform in flat, monoclinic rhombohedra, m. p. 163—164° (decomp.). A quantitative yield of the same compound can be obtained by treating an alcoholic solution of hydroxydimethylhydantoincarbamide with hydrogen chloride.

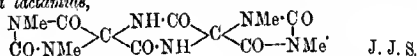
When boiled with water, the dimethylcaffolide takes up a molecule of water and loses carbon dioxide, yielding 1:3-dimethylhydantoinamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{C}(\text{OH}) \begin{array}{l} \text{NMe} \cdot \text{CO} \\ \text{CO} \cdot \text{NMe} \end{array}$ , which crystallises in large, mono-

or tri-clinic prisms, m. p. 180—182° (decomp.). The ethyl ether,

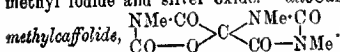


obtained by saturating the alcoholic solution with hydrogen chloride, crystallises in six-sided prisms, m. p. 189°—190°, and the *diacetyl* derivative,  $C_{10}H_{13}O_6N_3$ , crystallises in flat, rectangular prisms, m. p. 172°—173°.

Cholesterophan is formed when 5-hydroxy-1:3-dimethylhydantoyl-amide is oxidised with nitrous acid or with dichromate and sulphuric acid, and also when the amide is distilled. Mesoxalic acid and dimethylcarbamide are formed when the amide is boiled with barium hydroxide solution. Hydrogen peroxide and ammonia react with the amide, yielding cholesterophan and formic acid. When heated at 210°, the amide loses carbon dioxide and yields a product, m. p. 330° (decomp.), which is regarded as 5-hydroxy-1:3-dimethylhydantoin-5-carboxylic acid lactamide,



Degradation of Tetramethyluric Acid. *alloCaffeine*. HUNNICH BILTZ (*Ber.*, 1910, 43, 1600—1618. Compare Schmidt and Schilling, *Abstr.*, 1885, 995; Fischer, *Abstr.*, 1898, i, 180; Torrey, *Abstr.*, 1899, i, 86).—The constitution of *allocaffeine* has been established by its synthesis from 1:3-dimethylcaffolide (compare preceding abstract) by the methylation of the *silver* salt,  $C_8H_6O_6N_2Ag$ , and by means of methyl iodide and silver oxide. *alloCaffeine* is therefore 1:3:7-tri-



The degradation of tetramethyluric acid to *allocaffeine* probably proceeds in the following stages: (1) Oxidation to the corresponding glycol; (2) rupture of the alloxan ring at position 3:4, and formation of 5-hydroxy-1:3-dimethylhydantoyl-7:9-dimethylcarbamide; (3) hydrolysis to methylamine and the hydroxy acid; (4) elimination of water and formation of the lactone.

Attempts have been made to prepare tetramethyluric acid glycol by the condensation of dimethylalloxan with dimethylcarbamide, but the reaction proceeds further, and methylamine and *allocaffeine* are the only products obtained. This method is the most convenient for the preparation of *allocaffeine*, especially when the condensation is carried out in the presence of dilute hydrochloric acid (1:2) at the ordinary temperature, as under these conditions a 95% yield of *allocaffeine* is obtained at the end of two days. *alloCaffeine* can also be obtained by the condensation of methylalloxan with dimethylcarbamide, and by the methylation of 5-hydroxy-1:3-dimethylhydantoylcarbamide (preceding abstract) with methyl sulphate.

*alloCaffuric acid*, obtained by boiling an aqueous solution of *allocaffeine* (Torrey, *loc. cit.*), has m. p. 168.5°—169.5° after it has been once fused. This method of formation is analogous to the conversion of 1:3-dimethylcaffolide into 5-hydroxy-1:3-dimethylhydantoylamide (preceding abstract). *alloCaffuric acid* is therefore 5-hydroxy-1:3-dimethylhydantoylmethylamide,  $\text{NHMe} \cdot \text{CO} \cdot \text{C}(\text{OH}) < \begin{array}{c} \text{NMe} \cdot \text{CO} \\ \diagdown \\ \text{CO} \cdot \text{NMe} \end{array}$ , and its reactions are in complete harmony with this constitution. When

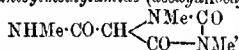
distilled, it yields cholesterol and methylformamide, and when hydrolysed with barium hydroxide yields methylamine, mesoxalic acid, and dimethylcarbamide.

5-Acetylallocaffuric acid,  $C_9H_{13}O_5N_3$ , crystallises in well-developed twinned prisms, m. p. 194.5–195.5°. The ethyl ether, 5-ethoxy-

1:3-dimethylhydantoinmethylamide,  $NHMe \cdot CO \cdot C(OEt) \begin{matrix} \nearrow NMe \cdot CO \\ \searrow CO - NMe \end{matrix}$ ,

obtained by saturating an alcoholic solution of the hydroxy-compound with hydrogen chloride at 0°, crystallises in well-developed, monoclinic prisms, m. p. 112–113°. The corresponding methyl ether,  $C_9H_{13}O_5N_3$ , has m. p. 121–122°.

1:3-Dimethylhydantoinmethylamide (deoxyallocaffuric acid),



obtained by reducing allocaffuric acid with hydriodic acid ( $D = 1.96$ ), crystallises from alcohol in flat prisms, m. p. 180°, after sintering at 170°, and can be oxidised by chlorine water to allocaffuric acid.

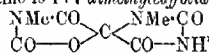
alloCaffeine reacts with a cold 33% alcoholic methylamine solution, yielding allocaffuric acid and dimethylcarbamide. The reaction probably consists in the addition of methylamine to the allocaffeine, yielding 5-hydroxytetramethylhydantoincarbamide, which at once reacts with methylamine, forming allocaffuric acid and dimethylcarbamide. Methylamine and ammonia react in a similar manner.

Schmidt and Schilling's caffeinemethylhydroxide (*loc. cit.*) is to be

represented by the formula:  $CO \begin{matrix} \nearrow NMe \cdot CO \cdot C \cdot NMe \\ \searrow NMe - C \cdot NMe(OH) \end{matrix} \rightarrow CH$ .

J. J. S.

apoCaffeine and the Degradation of 1:3:7-Trimethyluric Acid and of Caffeine. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1910, 43, 1618–1632. Compare Fischer, *Abstr.*, 1882, 217, 628; 1897, i, 267–268).—apoCaffeine is 1:7-dimethylcaffolide,



as its silver salt,  $C_7H_9O_5N_3Ag$ , yields allocaffeine when treated with silver oxide and methyl iodide. Similarly, caffuric acid is 5-hydroxy-1-methylhydantoinmethylamide, as it yields allocaffuric acid when methylated.

The best method of obtaining apocaffeine is the oxidation of caffeine with potassium chlorate and concentrated hydrochloric acid (compare Maly and Andreasch, *Abstr.*, 1882, 629). When dilute hydrochloric acid is used, and excess of acid is avoided, an isomeride, isoapocaffeine, is also formed; the proportions are apocaffeine four-fifths, and the iso-compound one-fifth. The same iso-compound is also formed by the action of potassium chlorate and hydrochloric acid on trimethyluric acid or on chlorocaffeine. It crystallises in four-sided pyramids or in lancet-shaped plates, decomposes at 176–177°, and when methylated yields allocaffeine. apoCaffeine and isoapocaffeine can be synthesised from methylcarbamide and dimethylalloxan in hydrochloric acid solution, and this appears to be the most convenient



method for the preparation of *apocaffeine*; a trimethyluric acid glycol could not be isolated.

The *ethyl ether* of *caffuric acid*, 5-ethoxy-1-methylhydantoinmethylamide,  $\text{NHMe} \cdot \text{CO} \cdot \text{C}(\text{OEt}) \begin{matrix} \text{NMe} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{matrix}$ , crystallises in compact prisms, m. p. 220—221°. J. J. S.

**Carbon-Nitrogen Linkings.** HEINRICH BILTZ (*Ber.*, 1910, 43, 1632—1636).—It is pointed out that the affinities existing between nitrogen and carbon are analogous to the affinities which take part in salt formation.

The compounds formed increase in stability as the basic nature of the nitrogen and the acidic nature of the carbon are increased and vice versa. This accounts for the stability of the glycols formed from 7 and 9 alkylated uric acids. Such compounds when decomposed suffer rupture in the alloxan ring.

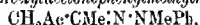
Noticeable is the fact that the introduction of methyl groups into the alloxan ring facilitates decomposition to such an extent that it has not been found possible to isolate the glycols of tri- and tetramethyluric acids.

Similar relationships are met with in the glycols derived from diphenylglyoxalones. Various other examples are cited. J. J. S.

**Dihydrazines.** III. JULIUS VON BRAUN (*Ber.*, 1910, 43, 1495—1505. Compare *Abstr.*, 1908, i, 700, 737).—4:4'-Bismethylhydrazinodiphenylmethane (diphenylmethanedimethyldihydrazine) reacts readily with diketones at the ordinary temperature, but only one carboxyl group takes part in the reaction.

Acetonylacetone and 2:9-decanedione (*Abstr.*, 1907, i, 893) yield thick, oily condensation products. Acetylacetone yields a product,  $\text{CH}_3(\text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{N} \cdot \text{CMe} \cdot \text{CH}_2\text{Ac})_2$ , m. p. 144°, and benzoylacetone, a product,  $\text{CH}_3(\text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{N} \cdot \text{CPh} \cdot \text{CH}_2\text{Ac})_2$ , which crystallises in yellow plates, m. p. 147°. Diacetyl yields a product which melts at about 100°.

Contrary to Kohlrausch's statement (*Abstr.*, 1890, 24), it is found that *asphenylmethylhydrazine* also reacts readily with diketones in acetic acid solution. *Acetylacetonephenylmethylhydrazone*,



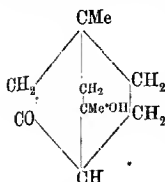
forms long, prismatic crystals, m. p. 98°, and b. p. 165°/12 mm.; the benzoylacetonephenylmethylhydrazone has m. p. 80°, not 103—104°.

Cyclic ketones containing the group  $-\text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2-$ , and in addition several side-chains, react with the dihydrazine and a little sulphuric acid in the same manner as the ketones described previously (*Abstr.*, 1908, i, 737), but not quite so readily; in each case ammonia is evolved, and an amorphous carbazole condensation product sparingly soluble in alcohol is obtained.

Ethyl 1-methylcyclohexan-5-one-2-carboxylate yields a product, which on hydrolysis gives an acid decomposing at about 200°. The acid, obtained by hydrolysing the condensation product from ethyl 1:3-dimethylcyclohexan-5-one-2-carboxylate, has m. p. 171°. Dihydroisophorone yields a product, which sinters at 167° and melts at 180°;

ethyl dihydroisophoronecarboxylate, a *product*, m. p.  $102^{\circ}$ ; and ethyl 1-phenylcyclohexan-3-one-5-acetate, a *product*, which melts at  $175^{\circ}$  after sintering at  $155^{\circ}$ .

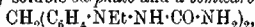
Carvone, thujone, diosphenol, and dimethyldicyclononanone (Rabe, Abstr., 1908, i, 554) do not react with the dihydrazine. The non-



reactivity of the last-mentioned compound indicates that its constitution is probably that of a dicyclooctane derivative (annexed formula).

Arabinose, rhamnose, galactose, and mannose react readily with the dihydrazine. Ketoses, dextrose, xylose, glucosamine, lactose, maltose, raffinose, and sucrose do not react. This difference is undoubtedly due to spatial relationships of the hydroxyl groups. The hydrazones formed from arabinose, rhamnose, galactose, and *d*-mannose are obtained in theoretical amount, and can be readily isolated from aqueous alcoholic or dilute acetic acid solutions, as they are sparingly soluble. The products melt respectively at  $180^{\circ}$  (decomp.),  $163^{\circ}$ ,  $185^{\circ}$ ,  $179^{\circ}$ . Mixtures of mannose and dextrose and of arabinose and xylose can be separated easily by means of the different behaviour of the sugars towards the dihydrazine.

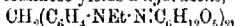
Diphenylmethanediethyldihydrazine,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{NH}_2)_2$ , is an oil; it yields a sparingly soluble *sulphate* and a *semicarbazide*,



obtained by the action of potassium cyanate, m. p.  $215^{\circ}$ .

The diethyldihydrazine yields hydrazones with aromatic aldehydes, which can be obtained in a crystalline form from pyridine. Benzaldehyde yields a *product*,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{N}\cdot\text{CHPh})_2$ , in the form of colourless, glistening plates, m. p.  $161^{\circ}$ ; anisaldehyde, a *product*,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , m. p.  $142^{\circ}$ ; glyoxal yields a solid *hydrazone*,  $\text{CH}_2\begin{matrix} \text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{N}\cdot\text{CH} \\ \text{C}_6\text{H}_4\cdot\text{NEt}\cdot\text{N}\cdot\text{CH} \end{matrix}$  but most aliphatic aldehydes yield

oily hydrazones. The sugars react somewhat more slowly with the diethyl compound. Mannose yields a *hydrazone*,



m. p.  $183^{\circ}$ .

J. J. S.

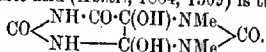
**Behaviour of Certain Ureides and Purine Substances towards Sodium Benzoate Solutions.** GIOVANNI PELLINI and MARIO AMADORI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 480—487).—The authors have measured the variations produced in the freezing points of water and of solutions of sodium benzoate of a number of different, fixed concentrations by the addition of increasing quantities of certain ureides and purine derivatives (compare this vol., i, 416). The results show that carbamide and urothane behave normally in water and in sodium benzoate solutions. Diethylbarbituric acid ("veronal") gives normal depressions of the freezing point of water, and even with concentrated solutions of sodium benzoate there is neither an appreciable increase of solubility nor sufficient variation of the freezing point to indicate the formation of a compound between the veronal and sodium benzoate. Alloxan behaves normally in water, but forms a

compound with sodium benzoate; allantoin exhibits similar behaviour. The slight solubility of uric acid in water does not appear to be increased in presence of sodium benzoate, whilst the solubility of theochromine is apparently augmented to some extent. Theophylline increases in solubility in presence of sodium benzoate.

No clear relation exists between the dissociation constants of these different compounds and their tendencies to form complexes with sodium benzoate, although caffeine has the smallest dissociation constant and the greatest capacity for complex formation.

T. H. P.

**Uric Acid Glycols.** HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1910, 43, 1511—1519).—A comparison of the formulae of 7:9-dimethyluric acid and 1:3-dimethyl-4:5-diphenylglyoxalose and their oxidation (*Abstr.*, 1908, i, 218) points to the conclusion that Fischer's oxy-7:9-dimethyluric acid (*Abstr.*, 1884, 1309) is the glycol:



This view is shown to be correct, as Fischer's compound can be synthesised by heating together alloxan and dimethylcarbamide, either alone or in acetic acid or concentrated aqueous solution. These methods are much more convenient than Fischer's for the preparation of the glycol. When its solution in glacial acetic acid is heated for a long time, an isomeride is formed. The crystals of the glycol are triclinic, and show cleavage along the base; the angle  $b:a=96^\circ$ ,  $c:a=98^\circ$ , and  $a:b=99^\circ$ .

Methylcarbamide and alloxan yield a *methyluric acid glycol*,  $\text{C}_8\text{H}_8\text{O}_5\text{N}_4$ , which crystallises in flat prisms or plates, m. p.  $208-209^\circ$  (decomp.), and it is not so soluble as the dimethyl derivative.

7:9-Diethyluric acid glycol,  $\text{C}_9\text{H}_{11}\text{O}_5\text{N}_4$ , crystallises in monoclinic prisms, begins to melt at  $105^\circ$ , and becomes quite clear at  $120^\circ$ .

Ethyluric acid glycol,  $\text{C}_7\text{H}_{10}\text{O}_5\text{N}_4$ , crystallises in glistening plates, which decompose at  $198-200^\circ$ .

J. J. S.

**Hexanitrohydrazobenzene and Salts of Trinitrodiphenylamine.** ARTHUR HANTZSCH and JOSEPH LISTER (*Ber.*, 1910, 43, 1685—1688).—When a solution of hexanitrohydrazobenzene in methyl alcohol or acetonitrile is evaporated in a desiccator, a residue is obtained of the yellow, real hexanitrohydrazobenzene, together with a red mass which probably consists of a compound of the *aci*-nitro-form and the solvent, since by warming or by treatment with acids the red mass loses weight and changes into yellow hexanitrohydrazobenzene. This view is supported by spectrometric evidence. Yellow solutions of hexanitrohydrazobenzene show only general absorption, whilst red solutions yield absorption spectra very similar to those of the alkali salts of the hexanitro-compound.

C. S.

**The Refractive Indices of Solutions of Certain Proteins.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, 7, 359—364).—If  $n$  is the refractive index of the solution,  $n_s$  of the solvent (distilled water, 1.3333 at  $18^\circ$ ),  $c$  the percentage concentration of the protein, and  $a$  a constant equal to the change in the refractive index produced by

dissolving 1 gram in 100 c.c., then  $n - n_1 = ac$ . The values of  $a$  for ovomucoid, ovo-vitellin, and caseinogen respectively are 0.00160, 0.00130, and 0.00152. W. D. H.

**Adsorption Compounds of Certain Proteins with Inorganic Haloid Salts Soluble in Alcohol.** FRIEDRICH SIMON (*Zeitsch. physiol. Chem.*, 1910, 66, 70—87).—Certain haloid salts (calcium chloride, bromide and iodide, strontium chloride, and lithium chloride) which are soluble in alcohol, when mixed with proteins and protein digestion products in aqueous solutions are precipitated with the proteins in definite quantities on the addition of alcohol. The removal of the salts by washing or by re-solution and precipitation is very difficult and never complete. The precipitates form brown powders on drying, which dissolve easily in warm water; the solutions exhibit the typical reactions of the anions and cations of the salts used; these are present in the same proportions as in the salts. W. D. H.

**Calorimetric Investigations of the Precipitation of Proteins by Salts of Heavy Metals.** TULLIO GAYDA (*Biochem. Zeitsch.*, 1910, 25, 341—358).—The author determined the heat of reaction when salts of heavy metals in varying strengths of solution are added to protein solutions, and by analysis, the composition of the precipitate formed. If a precipitate is formed in the case of copper salts, there is a fall of temperature. This is the algebraical sum of the heat of solution and the heat of precipitation, which latter factor is negative. This latter is itself the algebraical sum of the heat of precipitation of protein (0.4025 cal. for 1 gram protein, which number is independent of the protein concentration in solution) and the heat of adsorption of copper sulphate by the protein (—20.1621 cal. for 1 gram of copper sulphate). In greater concentrations, when no precipitate is formed, the heat of reaction is the algebraical sum of the heat of dilution of the copper sulphate solution and a residual heat which is negative, and which indicates that even when no precipitate is formed, a complex of protein and copper sulphate is formed. When a precipitate is formed by mercuric salts, the heat of reaction is positive. The conditions here are somewhat more complex than in the case of copper salts, as the heat of adsorption of mercury salts by the protein complex is a function of two variables; namely, the quantity of protein precipitated and the mercury salt carried down with this precipitate. The heat of adsorption of 1 gram of mercuric chloride is a parabolic function of the quantity of protein precipitated. S. B. S.

**A Protein Substance in the Pancreatic Juice.** ELKAN WACHSLER (*Zeitsch. physiol. Chem.*, 1910, 66, 284—286).—The protein in pancreatic juice is not a nucleo-protein, nor a gluco-protein. It gives Millon's and the biuret reactions. It contains 13.2% nitrogen. It yields in parts % of the total nitrogen: ammonia, 0.3; humin I, 10.9; humin II, 5.4; histidine, 4.1; arginine, 15.7; lysine, 1.3; and mono-amino-acids, 56.9. In parts % of the total protein, the following figures are given: arginine, 6.44; histidine, 1.99; lysine, 0.89; ammonia, 0.05. It is thus poor in lysine, and very poor in ammonia. W. D. H.

**Rate of Solution of Casein in Solutions of the Hydroxides of the Alkalis and of the Alkaline Earths.** T. BRAILSFORD ROBERTSON (*J. Physical. Chem.*, 1910, 14, 377—392. Compare also *Abstr.*, 1908, i, 930).—When casein is stirred at an approximately constant rate in solutions of the hydroxides of the alkalis or of the alkaline earths, the amount dissolved is given by the equation  $x = kt^m$ , where  $x$  is the number of grams of casein dissolved,  $t$  is the time which has elapsed since the casein was introduced into the solvent, and  $k$  and  $m$  are constants depending on the concentration and nature of the hydroxide solution and on the total mass of casein in the mixture.

Within the errors of experiment, the rapidity of solution is not affected by the temperature for temperatures ranging between room temperature and 30°.

Equally concentrated solutions of the hydroxides of potassium, sodium, lithium, and ammonium dissolve casein at approximately the same rate. Solutions of the hydroxides of the alkaline earths dissolve casein much more slowly, strontium hydroxide dissolving it the most, and barium hydroxide the least, rapidly.

The amount of casein dissolved by a solution of potassium hydroxide in a given time is directly proportional to the concentration of the hydroxide.

The velocity of solution of the casein increases with the mass of casein present in the mixture. The rate of increase of the velocity of solution with increasing mass of the casein is at first rather large, but it becomes much less as the mass of the casein is still further increased.

In the light of the above results, it is suggested that the factor which determines the rate of solution of casein in the alkaline solutions mentioned is the velocity with which the casein particles are penetrated and moistened by the solvent.

T. S. P.

**Partial Hydrolysis of Casein.** ZDENKO H. SKRAUP and E. KRAUSE (*Monatsh.*, 1910, 31, 149—163. Compare Skraup and Hummelberger, *Abstr.*, 1908, i, 711; Skraup and Woerber, *ibid.*, 1909, i, 446; Skraup and Lampl, *ibid.*, i, 537).—The products obtained by shaking casein with 60% sulphuric acid have been examined. It has been found possible to isolate a product very sparingly soluble in water, and resembling casein in many respects; this is termed albumose I. Among the products precipitated on the addition of ammonium sulphate, the one obtained when the solution is one-fourth saturated is formed in appreciable amount and is termed albumose II. A product which is not precipitated by ammonium sulphate is termed peptone. All three products were hydrolysed with concentrated hydrochloric acid, and the amounts of tyrosine and glutamic acid determined. The peptone did not yield any tyrosine, but the two albumoses gave somewhat larger yields than the casein itself. Albumose II gave far less glutamic acid than the original casein, whereas the peptone gave much the same amount, and albumose I somewhat more. The following colour-reactions of the three products were also examined: Millon's, oxylic acid, biuret,  $\beta$ -naphthol, and thymol.

J. J. S.

**Cleavage Products obtained by the Partial Hydrolysis of Proteins.** EMIL ABDERHALDEN and AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1910, 68, 13—18).—From Canton silk, glycyl-*d*-alanine anhydride and glycyl-*L*-tyrosine anhydride were obtained. From Neuchang silk and Indian tussore, *d*-alanine anhydride and glycyl-*d*-alanine anhydride were obtained. By the partial hydrolysis of *Italiao grège* and Canton silk, alanine anhydride was not obtained.

W. D. H.

**Blood Colouring Matter.** WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1910, 68, 165—249. Compare this vol., i, 210).—Dehydrochloridehæmin undergoes changes on keeping which hinder the simple addition of hydrogen chloride and reformation of hæmin. Hæmin crystals are obtained from dehydrochloridehæmin by the action of hydrochloric acid, but hæmatin prepared by the action of alkalis on hæmin does not behave similarly. Hæmin dissolves both in aniline and in *p*-toluidine, owing to salt formation, but not in *o*-toluidines; this is ascribed to steric hindrance.

In the preparation of hæmatoporphyrin any oxidation in acid solution is to be avoided, and therefore sulphuric or hydrochloric acid should not be used. The iron eliminated is tervalent. Hæmin is more resistant to acids than hæmatin or dehydrochloridehæmin. Acetic acid acts but weakly on hæmatin, even at high temperatures.

Hæmin and hæmatin are insoluble in acid carbonates and diacid phosphates; with normal carbonates, acid carbonates are formed. The disodium salt of hæmatin gives up a molecule of sodium hydroxide on prolonged dialysis. Solutions of the alkali salts of hæmatin polymerise on keeping.

Precipitates obtained with metallic salts have not the exact composition:  $C_{84}H_{20}O_4MN_4FeOH$ . In the iron and silver salts, the metal seems to be fixed in a complex salt, and in such salts the attachment of the iron in hæmatin is rendered looser.

Typical hæmin is not obtained by Eppinger's method, and only in admixture with another substance by Sievert's method. The longer hæmatin remains in alkaline solution, the more difficult it is to prepare typical hæmin from it. The solution of hæmatin obtained by decomposing the hæmin compound with sulphuric acid and alcohol, when treated with hydrochloric acid at 50—72° gives a product soluble in alkali, but at 80° an insoluble product partly esterified is produced.

In hæmin the group  $>FeCl$ , in hæmatin  $>FeOH$ , replace the imide hydrogen of the pyrrole ring; the acid properties of the two substances are due to the presence of two carboxyl groups. In passing into dehydrochloridehæmin, hydrogen chloride is eliminated between two of these and the group  $>FeCl$ . In the reduction of hæmatin to hæmochromogen, ferric are reduced to ferrous compounds. The addition of carbon dioxide to hæmochromogen, or of oxygen, carbon dioxide or nitrous oxide to hæmoglobin, takes place at the iron. E. F. A.

**The Non-Existence of "Protagon" in the Brain.** OTTO ROSENHEIM and M. CHRISTINE TEBB (*Biochem. Zeitsch.*, 1910, 25, 151—160).—The authors maintain, in opposition to Wilson and

Cramer, that the so-called "protagon" is not a simple substance. A product can be obtained which on repeated recrystallisation from small quantities of alcohol does not vary very appreciably in composition; if, however, larger quantities of alcohol or other solvents be employed for recrystallisation, the "protagon" can be separated into fractions of varying composition, especially as regards the phosphorus content (from 0.07 to 3.13%). The authors give some details as to the composition of fractions obtained in various recrystallisations.

S. B. S.

Some Colloid-Chemical Aspects of Digestion with Ultra-microscopic Observations. JEROME ALEXANDER (*J. Amer. Chem. Soc.*, 1910, 32, 680—687).—After drawing attention to the fact that the catalytic action of enzymes probably depends on the preliminary formation of a compound of the enzyme with the substrate, it is pointed out that this product is most likely a colloidal absorption compound, and it is suggested that enzymes produce their effects by virtue of their specific surface actions and the motion of their particles. This view has been confirmed by observations with the ultramicroscope. When starch grains were treated with a solution of diastase, ultramicros in rapid motion were seen to accumulate about the starch grains, which after a time showed an indented outline. The bright appearance of the field indicated the presence of numerous finer particles, whilst some particles of an intermediate size were visible. A solution of egg-albumin which had been heated nearly to boiling was opalescent, and, when viewed with the ultramicroscope, presented a field full of bright and rapidly moving ultramicros. On adding a pepsin solution containing 15% of alcohol, immediate coagulation took place. On addition of dilute hydrochloric acid, the coagulated masses became disintegrated, and ultramicros again appeared as before. The albumin particles gradually decreased in size, and eventually disappeared.

Reference is made to the action of reversible colloids in protecting irreversible or unstable colloids from coagulation, and consequently enabling colloidal sols to pass through membranes otherwise impermeable to them. This principle of colloidal protection has been demonstrated with the aid of the ultramicroscope. The casein particles in milk are seen to be in active motion, but if dilute acid is added, they immediately coagulate. If, however, a little gelatin or gum arabic is introduced before acidifying, coagulation is prevented, and the casein particles continue in motion. Gelatin exerts a greater protective action than gum, and is able to protect casein from coagulation by rennin.

E. G.

The Fatal Temperature for Plant Tyrosinases. GABRIEL BERTRAND and M. ROSENBLATT (*Compt. rend.*, 1910, 150, 1142—1145; *Bull. Soc. chim.*, 1910, [iv], 7, 557—561. Compare Abstr., 1907, i, 811).—The view that more than one specific tyrosinase exists gains support from the fact that some enzymes of this type are more resistant to heat than others. The temperature at which the enzyme ceases to be capable of developing a coloration with tyrosine

has been determined for a number of preparations of different origin. Thus the fatal temperature for the tyrosinase from *Amanita rubescens* is 60—65°; from *Russula queletii*, *R. rubra*, and *R. delica*, 65—70°; from lentils and potatoes, 80—85°, and for that from the root of beetroot, 90—95°. The temperature for any particular enzyme is only slightly influenced by the nature of the solvent and the mode of preparation; furthermore, in mixtures containing more than one, each diastase behaves as if the others were absent. W. O. W.

**Action of Hypophosphorous Acid on Dinaphthapyranol, Dinaphthapyrylphosphinous Acid.** ROBERT FOSSE (*Bull. Soc. chim.*, 1910, [iv], 7, 357—359).—Dinaphthapyrylphosphinous acid, the formation of which has been described already (this vol., i, 292), forms small, white crystals, which develop a superficial reddish-violet coloration, and in alcoholic solution reduces silver nitrate. The sodium salt forms brilliant silvery crystals from water, which become opaque on drying, and gradually develop a reddish-violet tint. The barium salt separates in crystals from hot water. T. A. H.

**Preparation and Properties of *p*-Iodophenylarsinic Acid and Certain of its Derivatives.** I. EFISIO MAMELI and ALDO PATTI (*Gazzetta*, 1910, 40, i, 128—137).—Part of the work here described has been already published (*Abstr.*, 1909, i, 543).

*p*-Iodophenylarsenious oxide,  $C_6H_4I \cdot AsO$ , obtained, together with hydriodic acid, by the action of water or an alkali carbonate or hydroxide on *p*-iodophenylarsenious iodide (*loc. cit.*), forms a straw-coloured powder, m. p. 245—250°.

*p*-Di-iodoarsenobenzene,  $C_6H_4I \cdot As \cdot As \cdot C_6H_4I$ , prepared by reducing *p*-iodophenylarsinic acid by means of phosphorus acid, is a yellow substance, m. p. 145—150°, insoluble in all organic solvents.

T. II. P.

**Preparation of Homologues of *p*-Aminophenylarsinic Acid.** FAREWERKE VOM MEISTER, LUCIUS & BRÜNING (D.R.-P. 219210).—In the well-known preparation of magenta by heating *o*- and *m*-toluidines with arsenic acid, the latter acts simply as an oxidising agent; the methods are now described by which it is induced to become a substituting agent.

*o*-Toluidine (90 parts) is heated in a distilling apparatus, and finely-powdered arsenic acid (24 parts) slowly stirred in, the temperature being maintained with continual stirring at 165—168° during about an hour, when water and *o*-toluidine distil over; the internal temperature is then raised to 185—190° during an equal period, the apparatus cooled, and the contents treated with water, rendered alkaline with calcium or barium hydroxide, and any residual toluidine removed with steam. The liquid is saturated with sodium chloride, and, after twenty-four hours, filtered, and the liquid just acidified with hydrochloric acid, when a resinous by-product separates, and, after a further twenty hours, the pure 4-amino-3-tolylarsinic acid is precipitated in needles, m. p. 194—195°. The sodium salt is crystalline, and can be separated from its aqueous solution by addition of alcohol.



4-Amino-2-tolylarsinic acid, m. p. 186°, is similarly prepared from *p*-toluidine.

4-Amino-2:5-xylylarsinic acid, from *p*-xylidine, crystallises with  $11\text{H}_2\text{O}$ , and when anhydrous has m. p. 215°. These compounds are colourless, and are readily soluble in hot, sparingly in cold, water; they yield crystalline salts, and diazotise readily with nitrous acid; their therapeutic germicidal action is analogous to that of *p*-amino-phenylarsinic acid.

F. M. G. M.

Action of Organo-magnesium Compounds on Boron Trichloride, Sulphur Chloride, and on the Chloride and Esters of Sulphurous Acid. WILHELM STRECKER (*Ber.*, 1910, 43, 1131—1136).—When magnesium phenyl bromide reacts with boron trichloride, only one chlorine atom is replaced, so that the final product is always phenylboric acid (compare Khotinsky and Melamed, *Abstr.*, 1909, i, 864). This acid cannot be titrated in the ordinary way, but it is more dissociated than boric acid, the molecular conductivity at 25° being 0.133. On the assumption that the conductivity at infinite dilution is the same as that of benzoic acid, this gives a degree of dissociation of 0.00027 at 25°, while that of boric acid is 0.00012 (Walker and Cormack, *Trans.*, 1900, 77, 5).

Magnesium phenyl bromide reacts with sulphur chloride ( $\text{S}_2\text{Cl}_2$ ), yielding phenyl disulphide; diphenyl is also formed.

As a result of the action of magnesium phenyl bromide and magnesium benzyl bromide on thionyl chloride, the corresponding sulphoxides are formed, in addition to diphenyl and benzyl sulphide. With *s*-diethyl sulphite the same sulphoxides are obtained. *as*-Diethyl sulphite and magnesium phenyl bromide yield phenyl ethyl sulphone.

The action of magnesium ethyl iodide and magnesium phenyl bromide on benzene solutions of nitrogen chloride (Hentschel, *Abstr.*, 1897, ii, 447) was tried without result.

R. V. S.

Action of Thionyl Chloride on Organo-magnesium Compounds. VICTOR GRIGNARD and L. ZORN (*Compt. rend.*, 1910, 150, 1177—1179. Compare Strecker, preceding abstract).—Thionyl chloride resembles carbonyl chloride in its action on organo-magnesium compounds (*Abstr.*, 1903, i, 455). When 1 mol. of the chloride is employed with 2 mols. of an aromatic magnesium compound, a sulphinone is produced, whilst if a greater proportion (3 mols.) of the magnesium derivative is taken, a sulphonium complex, of the type  $\text{SR}_2\cdot\text{OMgX}$ , is formed. When X is an aliphatic radicle, this undergoes decomposition in two directions: (1)  $\text{SR}_2\cdot\text{OMgX} = \text{SR}_2 + \text{MgX}\cdot\text{OR}$ ; (2)  $\text{SR}_2(\text{OMgX})\cdot\text{C}_n\text{H}_{2n+1} = \text{SR}_2 + \text{MgX}\cdot\text{OH} + \text{C}_n\text{H}_{2n}$ .

From the magnesium derivative of bromoquinol dimethyl ether, a small quantity of bis-2:5-dimethylphenylsulphinone,  $[\text{C}_6\text{H}_3(\text{OMe})_2]\text{SO}$ , was obtained, in the form of small crystals, m. p. 124—125°.

W. O. W.

## Organic Chemistry.

**Purification and the Physical Constants of Some Organic Liquids.** JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1910, 24 244—268).—The author gives a general discussion of the precautions which are necessary in the purification of an organic liquid by fractional distillation. Twenty-five different compounds have been investigated, the criteria of purity being the boiling point and the density. In some cases the freezing point and the critical solution temperature in an inert solvent were also used as criteria.

The following table gives a summary of the results. In each case the  $\pm$  refers to variations in the last decimal place given.

Substance.	B. p. /760 mm.	$dt/dp$ for 10 mm.	$D_4^{20}$
isoPentane .....	27.95 $\pm$ 1	0.37	0.63942 $\pm$ 3
Ethyl bromide .....	38.40 $\pm$ 1	0.36	1.50138 $\pm$ 2
Ethylene dichloride .....	83.70 $\pm$ 1	—	1.28238 $\pm$ 2
Chloroform .....	61.20 $\pm$ 1	0.35	1.52635 $\pm$ 2
Carbon tetrachloride .....	76.75 $\pm$ 1	0.41	1.53255 $\pm$ 2
Carbon disulphide .....	46.25 $\pm$ 1	0.42	1.29272 $\pm$ 2
Acetonitrile .....	81.60 $\pm$ 1	0.30	0.80350 $\pm$ 1
Ethylamine .....	16.55 $\pm$ 1	0.28	0.70570 $\pm$ 10
Methyl alcohol .....	64.70 $\pm$ 1	0.30	0.81017 $\pm$ 8
Ethyl ether .....	34.60 $\pm$ 1	0.36	0.73627 $\pm$ 3
Acetone .....	56.10 $\pm$ 1	0.30	0.81249 $\pm$ 3
Methyl ethyl ketone .....	79.60 $\pm$ 2	0.38	0.82551 $\pm$ 1
Methylal .....	42.30 $\pm$ 2	0.40	0.88548 $\pm$ 2
isoButyric acid .....	154.35 $\pm$ 2	0.32	0.96819 $\pm$ 2
Methyl formate .....	31.75 $\pm$ 2	0.34	1.00840 $\pm$ 3
Ethyl acetate .....	77.15 $\pm$ 1	0.41	0.90476 $\pm$ 2
Ethyl propionate .....	99.10 $\pm$ 1	0.40	0.91245 $\pm$ 2
Toluene .....	110.70 $\pm$ 1	0.42	0.88448 $\pm$ 2
Chlorobenzene .....	132.00 $\pm$ 1	0.49	1.12795 $\pm$ 1
Bromobenzene .....	156.15 $\pm$ 1	0.53	1.52193 $\pm$ 1
Benzonitrile .....	191.30 $\pm$ 1	0.54	1.02278 $\pm$ 3
Nitrobenzene .....	210.85 $\pm$ 1	0.48	1.32290 $\pm$ 4
Aniline .....	184.40 $\pm$ 1	0.51	1.03895 $\pm$ 2
Anisole .....	153.80 $\pm$ 2	0.48	1.01237 $\pm$ 2
Pyridine .....	115.50 $\pm$ 1	0.44	1.00302 $\pm$ 2

T. S. P.

**The First Synthesis of Ethyl Alcohol.** RAPHAEL MELDOLA (*J. Soc. Chem. Ind.*, 1910, 29, 737—740).—An historical paper in which the author maintains his thesis that Henry Hennel was the first to synthesise ethyl alcohol (compare Berthelot, *Abstr.*, 1899, i, 471; Fritzsche, 1902, i, 657).

T. S. P.

**Molecular Compounds of Alcohol and Water.** T. FAWCETT (*Pharm. J.*, 1910, [iv], 30, 754—757).—This paper is largely the mathematical exposition of a theory proposed to explain the contraction occurring when ethyl alcohol and water are mixed. According to

the theory advanced, when ethyl alcohol and water combine the first compound formed is invariably  $(C_2H_5O)_{18}H_2O$ , which subsequently combines with successive molecules of water, forming an indefinite number of compounds. Further, that the formation of each molecular compound or "system" causes a definite contraction of the total volume, and that the contraction is proportional to the weight of the water in the equation:  $(C_2H_5\cdot OH)_9, H_2O + H_2O = (C_2H_5\cdot OH)_9, 2H_2O$ . From the latter it is deduced that the contraction  $^{(n)}$  resulting on the formation of the compound  $(C_2H_5O)_{18}, nH_2O$  from the compound  $(C_2H_5O)_{18}, (n-1)H_2O$  is equal to  $\{5.136n/(23+n) - 5.136(n-1)/(23+(n-1))\}$  of the volume of water added. The contractions  $^{(n)}$  produced by nine successive additions of 5/18 gram-molecules of water to 5 gram-molecules of ethyl alcohol were measured at 15.5° in an apparatus described. The observed contractions diminish from 0.221 for the first addition to 0.113 for the ninth, the calculated figures varying from 0.214 to 0.119, whilst the difference only amounts to 0.01 in three instances.

E. H.

$\alpha$ -Dialkyl- $\beta$ -keto-alcohols. EDMOND F. BLAISE and I. HERMAN (*Ann. Chim. Phys.*, 1910, [viii], 20, 173—194).—Recapitulates work recorded already in Abstr., 1907, i, 749; 1908, i, 78, 248, 319, 536; 1909, i, 85, and continues the work dealt with in Abstr., 1909, i, 632. The following data are new. Kling and Viard's statement (Abstr., 1904, i, 545) that tertiary alcohols are dehydrated at the boiling point of naphthalene could not be verified in the cases of trimethylcarbinol or  $\alpha$ -hydroxydiisopropyl ketone,  $CHMe_2\cdot CO\cdot CMe_2\cdot OH$ . The primary alcohol, *ethyl hydroxy-sec. butyl ketone*,  $OH\cdot CH_2\cdot CHEt\cdot COEt$ , b. p. 102.5°/13 mm., is also stable under these conditions.

$\alpha$ -Hydroxydiisopropyl ketone, the formation of which has been described already (Abstr., 1908, i, 319), furnishes a *p*-nitrophenylhydrazone, m. p. 127.5°, crystallising in yellow needles. Attempts to synthesise this hydroxy-ketone from ethyl  $\alpha$ -hydroxy-isovalerate by the action of magnesium methyl iodide resulted in the production of  $\beta$ , $\beta$ -dimethylpentane- $\beta$ -diol,  $CHMe_2\cdot CH(OH)\cdot CMe_2\cdot OH$ , m. p. 58°, which crystallises in colourless needles, and yields a monoacetyl derivative,  $CHMe_2\cdot CH(OAc)\cdot CMe_2\cdot OH$ , b. p. 88—89°/11 mm., and a phenylurethane, m. p. 127°. This glycol on oxidation with chromic acid gives a mixture of ketones, but no  $\alpha$ -hydroxydiisopropyl ketone. On dehydration with sulphuric acid, the glycol yields diisopropyl ketone (Abstr., 1904, i, 219).

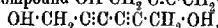
The following details are given of the compounds prepared in the course of the synthesis of ethyl tiglyl ketone (Abstr., 1908, i, 596):  $\beta$ -hydroxy- $\alpha$ -methylbutyric acid furnishes a phenylurethane, m. p. 128°, crystallising in slender needles. The acetyl derivative of the acid yields an ethyl ester, b. p. 97.5°/15 mm., a *p*-toluidide, m. p. 129°, slender needles, an  $\alpha$ -naphthylamide, m. p. 126°, and an acid chloride, b. p. 84°/13 mm. The last-mentioned substance condenses with zinc ethyl iodide to give  $\beta$ -acetoxy- $\alpha$ -methylpropyl ethyl ketone,  $OAc\cdot CHMe\cdot CHMe\cdot COEt$ ,

b. p. 97—97.5°/14 mm., and this on hydrolysis in the cold furnishes

mixture of the corresponding *hydroxy-ketone*, b. p. 89—90°/14 mm., and ethyl tiglyl ketone, b. p. 50·5°/13 mm.; the latter absorbs hydrogen-bromide, but the bromo-compound formed is unstable, and could not be isolated.

T. A. H. :

**Hydrogenation of Acetylenic Compounds.** ROBERT LESPIEAU (*Compt. rend.*, 1910, 150, 1761—1762).—Reduction of unsaturated glycols, such as the compound  $\text{OH}\cdot\text{CH}_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OH}$  or

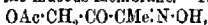


by means of platinum black and hydrogen in alcoholic or ethereal solution results in the production of a good yield of the corresponding saturated glycols. Small quantities of hexane and hexanol are also formed in the case of the latter compound. The yield is considerably diminished if the dimethyl ethers of the glycols are employed, owing to the formation of saturated hydrocarbons and of dimethyl ether.

W. O. W.

**Hydroxydiacetyl.** OTTO DIELS and MILAN FARKAS (*Ber.*, 1910, 43, 1957—1962).—It has not been found possible to obtain a monobromo-derivative of diacetyl, the only product formed by direct bromination being the dibromo-derivative (compare Fittig, Keller, and Daimler, *Abstr.*, 1889, 491). Diacetylmonoxime yields a monobromo-derivative when dissolved in methyl alcohol and treated with bromine at 0°, and this reacts with a methyl alcoholic solution of potassium acetate, yielding the corresponding acetyl derivative, which, when hydrolysed with barium hydroxide solution, yields the oxime of hydroxydiacetyl; but, so far, it has not been found possible to obtain hydroxydiacetyl itself.

Modifications of Diels and Jost's method (*Abstr.*, 1902, i, 744) for the preparation of diacetylmonoxime are recommended. Its bromo-derivative,  $\text{CH}_3\text{Br}\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , crystallises from benzene, has m. p. 83—84°, and attacks the mucous membrane. The *acetate*,



forms snow-white crystals, m. p. 93·5—94°. It yields a *phenylhydrazone*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , which forms sulphur-yellow, dichroic crystals, m. p. 132—133° (corr.).

*Hydroxydiacetylmonoxime*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , crystallises from water in large, brilliant prisms, m. p. 118·5—119·5° (corr., decomp.), and yields a *phenylhydrazine*,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CMe}\cdot\text{N}\cdot\text{OH}$ , which crystallises from alcohol in long, pale yellow, refractive needles, m. p. 97·5° (corr.).

*Hydroxydiacetylosazone*,  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{N}_2\text{HPh})\cdot\text{CMe}\cdot\text{N}_2\text{HPh}$ , obtained by the action of an excess of phenylhydrazine on a dilute acetic acid solution of the monoxime, crystallises in golden-yellow plates, m. p. 88° (corr., decomp.).

J. J. S.

**Attempts to Transform Nitrous Vapours into the Corresponding Calcium Salts by the Use of Ethyl Nitrite and Nitrate.** EUGÈNE TASSILLY and J. LEROIDE (*Bull. Soc. chim.*, 1910, vi, 7, 622—628).—Nitrous vapours are absorbed fairly completely by ethyl alcohol with the formation of ethyl nitrito and nitrate, but the resulting solution on treatment with lime does not furnish good

leads of the corresponding calcium salts, so that this method cannot be used for the conversion of waste nitrous fumes into calcium salts of industrial value.

Nitric oxide, obtained by the action of nitric acid on copper, was mixed with air, previously purified by passing over (1) pumice stone mixed with potassium hydroxide, and (2) pumice stone saturated with sulphuric acid, to form a mixture containing 1 to 2% of nitrous fumes, and this was drawn through alcohol kept at  $-20^{\circ}$ , then through glass-wool at  $-35^{\circ}$  to  $-40^{\circ}$ , to eliminate alcohol, etc., from the issuing gas, and finally through a tube containing diphenylamine in sulphuric acid. The last tube served as a test for nitrous vapours in the issuing gas, and its subsequent examination showed that the proportion of nitrous vapours which escaped absorption was less than  $1 \times 10^{-5}$  of that dissolved by the alcohol. The alcoholic solution at first contains ethyl nitrite and ethyl nitrate, but, when kept, part of the nitrate is hydrolysed, and the nitric acid formed reacts with the excess of alcohol to form acetaldehyde. Experiments on the hydrolysis of ethyl nitrite and nitrate in alcohol with potassium hydroxide showed that good yields of the potassium salts could be obtained, but with lime under similar conditions the hydrolysis of ethyl nitrite is negligible at atmospheric temperature or  $100^{\circ}$ , but amounts to 23.1% at  $140^{\circ}$ , and with ethyl nitrate amounts to 29.0 and 55.0% at  $140^{\circ}$  and  $150^{\circ}$  respectively. Potassium is not displaced from potassium nitrite or nitrate by boiling with lime in presence of alcohol. T. A. H.

**Ethyl Metaphosphate and its Use in Organic Chemistry.** KURT LANGHELD (*Ber.*, 1910, 43, 1857—1860).—*Ethyl metaphosphate*,  $C_2H_5PO_3$ , can be prepared by the action of ethyl iodide on silver metaphosphate, but is more readily obtained by the action of phosphoric oxide on anhydrous ethyl ether,  $OEt_2 + P_2O_5 = 2EtPO_3$ . It forms a thick syrup, and may be purified by solution in chloroform and precipitation with ether. It is readily hydrolysed by alkalis, and when boiled with ethyl alcohol gives a mixture of di- and tri-ethyl phosphates.

The metaphosphate when boiled with chloroform and dextrose yields two organic phosphorus compounds, from which crystalline barium salts have been obtained.

Leuciole reacts with a chloroform solution of ethyl metaphosphate yielding the compound:  $PO(OEt)(OH) \cdot NH \cdot CH(CO_2H) \cdot CH_2 \cdot CHMe_2$ .

The metaphosphate is a good condensing agent, as it eliminates water or ammonia very readily from mixtures of organic compounds. J. J. S.

**Formation and Decomposition of Thiols; Synthesis of Dialkyl Sulphides.** PAUL SANATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, 150, 1569—1572. Compare this vol., i, 456).—Attempts have been made to improve the yield of thiols from secondary alcohol when these are submitted to the catalytic process already described. Substitution of the oxides of zirconium, uranium, tungsten, chromium, molybdenum, or aluminium for the thorium oxide previously employed resulted in diminished yields in the case of isomyl alcohol and phenol.

Metallic sulphides have a catalytic effect on thiols precisely similar to that exercised by alumina on alcohols, and if cadmium sulphide is used, the reaction affords a convenient method for the preparation of dialkyl sulphides. When passed over this substance at 320–330°, ethyl hydrogen sulphide is converted into diethyl sulphide, whilst at 380° decomposition into ethylene and hydrogen sulphide occurs. With secondary thiols, the yield of dialkyl sulphide is smaller, and the tendency to undergo decomposition more marked. The reaction is represented as (1)  $\text{CdS} + 2\text{C}_n\text{H}_{2n+1}\cdot\text{HS} = \text{Cd}(\text{S}\cdot\text{C}_n\text{H}_{2n+1})_2 + \text{H}_2\text{S}$ ; (2)  $\text{Cd}(\text{S}\cdot\text{C}_n\text{H}_{2n+1})_2 = \text{CdS} + (\text{C}_n\text{H}_{2n+1})_2\text{S}$ . W. O. W.

Basic Ferric Acetate Contained in the Former Official Solution of Ferric Acetate. RUDOLF F. WEINLAND (*Arch. Pharm.*, 1910, 249, 337–345).—The addition of sodium platinichloride in slight excess to the former official solution of ferric acetate of the D.A.B. III causes a precipitation of the orange-red platinichloride,  $[\text{Fe}_2(\text{OH})_2] \frac{1}{2} \text{PtCl}_6 \cdot 5\text{H}_2\text{O}$ , described previously (*Abstr.*, 1909, i, 872). The basic acetate in the official solution, therefore, is the monoacetate,  $[\text{Fe}_2(\text{OH})_2] \text{OAc}$ . C. S.

Colloidal Properties of Soluble Soaps. FILIPPO BOTAZZI and C. VICTOROFF (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 659–665).—The soap employed consisted chiefly of sodium oleate with smaller quantities of palmitate, stearate, etc. When a concentrated solution of it is dialysed, the volume of liquid in the dialyser at first increases, and the clear solution becomes opalescent and finally milky. This is due to the gradual hydrolysis of the soap; the alkali formed diffuses out, and fatty acids and acid soaps are precipitated. At the end of the dialysis, the liquid forms three layers, two, at the surface and at the bottom respectively, consisting of the acids and the acid soaps, and a third, intermediate, milky layer, which is a microgranular suspension of these substances in a very dilute solution of soap. A small quantity of soap is also lost by diffusion during the dialysis. When examined electrically, both the soap and the granules in the dialysed liquid are found to move towards the anode. On adding water or small quantities of *N*/10-sodium hydroxide to the concentrated soap solution, a gradual decrease of the viscosity occurs. When *N*/10-sodium hydroxide is added to the turbid, filtered liquid, after dialysis, the viscosity at first increases, then decreases to its former value. If water is now added, the viscosity again slowly rises, owing to the decrease in concentration of the alkali present. The addition of an excess of sodium hydroxide causes precipitation of the soap. The concentrated soap solution has a very low surface tension, whilst that of the liquid after dialysis is not much less than that of distilled water. The variation of surface tension caused by addition of sodium hydroxide is similar to the changes produced in the viscosity, but in the reverse direction; when the viscosity increases the surface tension diminishes, and vice versa. R. V. S.

**Hydrolytic Decomposition of Aqueous Alcoholic Solutions of Alkali Soaps.** DAVID HOLDE [with H. DÖSCHER and G. MEYERHEIM] (*Zeitsch. Elektrochem.*, 1910, 16, 436—442).—When a solution of a soap in aqueous alcohol is made exactly neutral to phenolphthalein and then shaken with a solvent such as benzene, the solution becomes red and the benzene contains some of the fatty acid of the soap, showing that the neutral solution is hydrolysed to some extent. The hydrolysis diminishes as the concentration of the alcohol increases, and practically disappears in 80% alcohol. The bearing of this on the accuracy of titrations of fatty acids is discussed.

The partition of oleic acid between "benzine" and aqueous alcohol is also studied. With 40% alcohol, 99.8% of the acid passes into the "benzine."

T. E.

**Carbohydrate Esters of Higher Fatty Acids.** W. R. BLOOR (*J. Biol. Chem.*, 1910, 7, 427—430. Compare Neuberg and Pollak, this vol., i, 157).—Mannitol has been condensed with stearic acid under the influence of concentrated sulphuric acid at 65—75°, the mixture being then cooled and ether added (Grün's method).

A certain amount of ethyl stearate is formed as a by-product, and this complicates the purification of the condensation product. After repeated precipitation from its methyl alcoholic solution, *mannide distearate*,  $C_6H_5O_2(C_{18}H_{35}O_2)_2$ , was obtained as a colourless, semi-translucent, amorphous mass, which crystallised from ether in microscopic needles, m. p. 51°. It has  $[\alpha]_D^{20} + 63.9^\circ$ , and is readily hydrolysed by alcoholic sodium hydroxide solution.

J. J. S.

**Ester Condensation: Ethyl Oxalate and Propionitrile.** WILHELM WISLIGENUS and WILHELM SILBERSTEIN (*Ber.*, 1910, 43, 1825—1836).—The ordinary Claisen condensation (ethyl acetoacetate formation) is termed *ester condensation*. Three factors are of importance: the ester, the methylene derivative, and the condensing agent. According to Claisen the ester first forms an additive compound with the sodium alkoxide. The most reactive ester is ethyl oxalate, then follow ethyl formate, nitrite, acetate, benzoate, and nitrate. The most reactive methylene compounds are benzyl cyanide, ketones, ethyl acetate, fluorene, etc. Freund and Speyer (Abstr., 1902, i, 584) have found that sodamide is a more effective condensing agent than sodium ethoxide. The authors recommend the use of potassium ethoxide in cases where sodium ethoxide gives but poor yields or produces no condensation at all; thus ethyl oxalate and propionitrile do not condense in the presence of sodium ethoxide (Fleischhauer, Abstr., 1893, 397), but with potassium ethoxide in the presence of anhydrous ether give an 83% yield of ethyl  $\beta$ -cyano- $\alpha$ -ketobutyrate after the mixture has been kept for three days at the ordinary temperature. The potassium compound,  $C_7H_9O_3NK$ , crystallises from alcohol in slender, colourless prisms, m. p. 162—163°, when freshly prepared. The salt is stable, is not hygroscopic, and is not decomposed by carbonic or acetic acids. The sodium salt is less soluble, and the silver and copper salts form precipitates. Ethyl phenylketobutyrate,  $CN \cdot CHMe \cdot CO \cdot CO_2Et$ , crystallises from benzene

in large, yellow prisms, m. p. 66–67° and b. p. 123°/17 mm. It dissolves to an appreciable extent in water, yielding acid solutions. When freshly liberated from its potassium salt, the ester gives a pale coloration with alcoholic ferric chloride, but the coloration increases with the time. This points to the liberation of the ketonic form and its gradual passage into the enolic form:  $\text{CN}\cdot\text{CMe}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$ .

The ammonium salt,  $\text{C}_7\text{H}_{12}\text{O}_5\text{N}_2$ , forms colourless crystals, m. p. 113–114°.

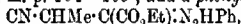
A 20% yield of  $\beta$ -cyano- $\alpha$ -ketobutyric acid (propionitrileoxalic acid),  $\text{CN}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , can be obtained by dissolving the ester in ether and a little alcohol, and passing in hydrogen chloride and shaking with a little water. It forms yellow needles, m. p. 207–208°.

When hydrolysed with 20% aqueous potassium hydroxide, the ester yields propionic and oxalic acids (acid hydrolysis), but when hydrolysed with 25% sulphuric acid the product is propionylformic acid, m. p. 151–152° (compare Wislicenus and Arnold, Abstr., 1888, 361) (ketonic hydrolysis).

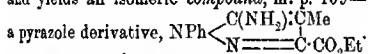
When warmed with dilute potassium hydroxide at 40°, or when treated with alkaline hydrogen peroxide at 40° (Radziszewski's method), the ester yields oxalpropionamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ ; this is best isolated as its phenylhydrazone,  $\text{C}_{11}\text{H}_{13}\text{O}_5\text{N}_3$ , which crystallises in glistening, colourless plates, m. p. 171–172°.

An 87% yield of the anil,  $\text{CN}\cdot\text{CHMe}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{NPh}$ , is obtained by gently warming the ester with aniline; it crystallises from ether in yellow, flat plates, m. p. 115–116°. If the mixture is heated for some time, aniline oxalate is formed.

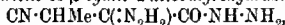
The ester yields an oxime,  $\text{CN}\cdot\text{CHMe}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{Et}$ , in the form of colourless prisms, m. p. 104–105°, and a phenylhydrazone,



in the form of yellow plates, m. p. 124–126°. The phenylhydrazone, when heated gradually to 200°, undergoes molecular rearrangement, and yields an isomeric compound, m. p. 109–111°, which is probably



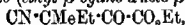
The ester reacts with an alcoholic solution of hydrazine hydrate, yielding the hydrazone of  $\beta$ -cyano- $\alpha$ -ketobutyrohydrazide,



which crystallises in colourless prisms, m. p. 190–192°.

When brominated in chloroform solution, the ester yields ethyl  $\beta$ -bromo- $\beta$ -carboxylamido- $\alpha$ -ketobutyrate,  $\text{NH}_2\cdot\text{CO}\cdot\text{CMeBr}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , which crystallises in colourless, slender prisms, m. p. 134–135°.

The potassium derivative of ethyl  $\beta$ -cyano- $\alpha$ -ketobutyrate, when boiled for several days with alcoholic ethyl iodide, yields ethyl  $\beta$ -cyano- $\beta$ -methyl- $\beta$ -ethylpyruvate (ethyl  $\beta$ -cyano- $\alpha$ -keto- $\beta$ -methylvalerate),



as a colourless oil, b. p. 130°/24 mm., which yields  $\alpha$ -methylbutyric acid when hydrolysed with potassium hydroxide solution and methyl-ethylpyruvic acid when hydrolysed with dilute sulphuric acid. The phenylhydrazone of the pyruvic acid has m. p. 132–133° (compare Locquin, Abstr., 1906, i, 929).



A cold solution of diazobenzene chloride reacts with the potassium salt of ethyl  $\beta$ -cyano- $\alpha$ -ketobutyrate, yielding the phenylhydrazone of acetyl cyanide (Favrel, *Bull. Soc. chim.*, 1902, [iii], 27, 194). The potassium salt reacts with *p*-nitrobenzoyl chloride, yielding the *p*-nitrobenzoyl derivative,  $\text{ON} \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , as colourless plates, m. p. 83–84°, which are readily hydrolysed.

J. J. S.

Cork. III. MAX VON SCHMIDT (*Monatsh.*, 1910, 31, 347–356, Compare Abstr., 1904, i, 501).—It has been shown previously that the extract of cork meal in chloroform or other indifferent solvent contains cerin and about 10% of glycerides, and that about 30% of fatty acids, but no glycerides, are obtained by heating the residue with alcoholic potassium hydroxide; hence the fatty acids in cork are not present as glycerides and are insoluble. Since they cannot be combined with the cerin, which would be found in the alcoholic solution if such were the case, it follows that they must be present as anhydrides or as insoluble polymerides. This conclusion is justified by experiments on phellonic acid—the acid obtained from cork which has been examined most thoroughly. When this acid is heated for fifty-four hours at the b. p. of xylene, or for six hours with fuming hydrochloric acid in a water-bath, it is converted into an *anhydride*, m. p. 102°, which, however, is soluble in chloroform and in benzene; hence this anhydride is probably present in cork, its non-extraction by chloroform being due to the fact that it is embedded in the insoluble constituents of the cork. If this is so, the crude fatty acids obtained from cork should yield an insoluble product by heating. Experiment proves this, for at 140° the crude acids are converted into a brown, elastic, transparent mass, which is insoluble in indifferent solvents and is impermeable by gases. In fact, by heating a mixture of the crude acids and an equal weight of sawdust at 140°, a product is obtained which closely resembles natural cork in colour, elasticity, and workability and other properties, and differs from it only by the absence of its characteristic structure.

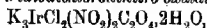
The substance to which the conversion of these fatty acids into an insoluble form is chiefly due is suberic acid, which is converted by heating, without loss of water and in the absence of air, into an insoluble, elastic mass, probably of a polymeride.

Cork, therefore, consists of an insoluble mixture of anhydrides and polymerides of solid and liquid fatty acids, together with the glycerides of these acids. Young cork most probably contains only glycerides, which in course of time, under the influence of air, light, and probably also of enzymes, are hydrolysed, the glycerol being oxidised to carbon dioxide and water; the fatty acids partly polymerising and partly forming anhydrides.

C. S.

#### Complex Iridium Derivatives. Iridiodichlorodinitro-oxalates.

MAURICE VÈZES and ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1910, [iv], 7, 507–512. Compare *Proc. verb. Soc. Sci. Bordeaux*, July 18, 1901).—*Tripotassium iridiodichlorodinitro-oxalate*,



obtained by boiling potassium irridiodichloro-oxalate (Z. anorg. Chem., 1909, i, 762) in concentrated aqueous solution with potassium nitrite, crystallises in orthorhombic, orange-yellow needles ( $a:b:c = 0.59101:1:0.81461$ ). It is stable at ordinary temperatures, loses  $2H_2O$  and becomes yellow at  $100-120^\circ$ , evolves nitrous fumes at  $250^\circ$ , and decomposes completely at  $375^\circ$ , leaving a black residue, having the shape of the original crystals and consisting of iridium, potassium chloride, and potassium nitrite. No deflagration occurs. The salt does not give reactions for chloride, nitrite, or oxalate.

The silver salt obtained by interaction between solutions of the potassium salt and of silver nitrate, the latter in excess, crystallises in anhydrous, microscopic, birefringent, bright yellow lamellae of rhombic form and having an acute angle  $65^\circ$ . The crystals give extinction with crossed nicols in a direction oblique to the diagonal. The salt is stable even above  $100^\circ$ , but begins to turn brown at  $120^\circ$ , and decomposes completely at  $260^\circ$ , but does not deflagrate. It undergoes double decomposition with hydrochloric acid or chlorides.

T. A. H.

**Complex Derivatives of Iridium.** Iridiodichlorodinitro-oxalic Acid and Salts. ALEXIS DUFFOUR (*Bull. Soc. chim.*, 1910, [iv], 7, 512-516).—The acid could not be isolated, but was obtained in solution by adding the equivalent amount of hydrochloric acid to the silver salt (see preceding abstract). This solution on evaporation even under reduced pressure evolved nitrous fumes, leaving eventually a black residue containing iridium. Salts of this acid can be prepared by (1) double decomposition with the potassium salt; (2) action of chlorides on the silver salt, or (3) by neutralisation of the aqueous solution of the acid. The salts have generally the properties recorded already for the potassium and silver salts (*loc. cit.*). They are very soluble in water, with the exception of the silver and thallous salts. Salts of the following metals were prepared: Rubidium, caesium, thallium, ammonium, lithium, and sodium. The last three crystallise with  $2H_2O$ . The hydrated ammonium salt is unstable and loses its water at atmospheric temperatures when kept over sulphuric acid, and some anhydrous crystals isomorphous with those of the rubidium salt separate with the hydrated salt in preparing the latter. The ammonium salt also differs from the others in deflagrating when heated.

T. A. H.

**By-Products Obtained During the Replacement of the Alkyl Groups in Ethyl Malonate.** TELEMACHOS KOMNENOS (*Monatsh.*, 1910, 31, 421-438).—It has been shown (this vol., i, 361) that methyl ethanetetra-carboxylate is the chief product obtained by the addition of iodine to the reaction product of ethyl malonate and sodium methoxide. The oily product of the reaction has now been examined. The portion which solidifies after a few days' keeping is probably methyl acetone-acry-tricarboxylate,  $CH(CO_2Me)_2 \cdot CO \cdot CH_2 \cdot CO_2Me$ , m. p.  $105-108^\circ$  (phenylhydrazone, m. p.  $125^\circ$ ), although its properties are not analogous to those of the ethyl ester described by Willstätter. The alcoholic mother liquor of the preceding ester contains a small quantity of

another substance,  $C_9H_{12}O_7$ , m. p.  $120^\circ$ , not identical with, but possibly the enolic form of, the preceding ester, and also a substance,  $C_{12}H_{16}O_8$ , m. p.  $75^\circ$  (*phenylhydrazones*, m. p.  $108-110^\circ$ ), which is probably methyl  $\gamma$ -hydroxyhexan- $\beta$ -dione- $\alpha$ - $\alpha$ -tricarboxylate, formed by the elimination of 2 mols. of methyl alcohol and 1 mol. of carbon dioxide from 2 mols. of methyl malonate and 1 mol. of methyl tartarate (which is produced by the action of iodine and water on methyl sodium-malonate).

The remaining oily portion of the original by-product is found to consist chiefly of an ester,  $C_9H_{12}O_7$ , m. p.  $97^\circ$  (*phenylhydrazones*, m. p.  $117-120^\circ$ ), which is isomeric, but not identical, with the ester first mentioned; it also contains an ester,  $C_{14}H_{18}O_{11}$ , m. p.  $85-87^\circ$ , which is probably methyl butan- $\gamma$ -one- $\alpha$ - $\beta$ - $\beta$ -pentacarboxylate, and also a very small quantity of an ester,  $C_{13}H_{16}O_8$ , m. p.  $85^\circ$  (*phenylhydrazones*, m. p.  $110^\circ$ ), which is possibly methyl hexan- $\beta$ -dione- $\alpha$ - $\alpha$ -tricarboxylate.

It is noteworthy that all the products obtained from ethyl malonate in the reaction under examination are methyl esters.

C. S.

**Acidity of Derivatives of Ethyl Oxalacetate.** HENRI GAULT (*Compt. rend.*, 1910, 150, 1608-1610).—The ethyl esters of the following acids may be titrated by alkalis, using phenolphthalein as indicator, in cold alcoholic or acetone solutions; the results obtained enable the molecular weights to be determined with a fair degree of accuracy: oxalacetic, oxalosuccinic,  $\alpha$ -oxaloglutamic, methylenedisoxalacetic, ethylenedisoxalacetic, propylenedisoxalacetic, heptylenedisoxalacetic, cyclopentan- $\beta$ - $\gamma$ -dione- $\alpha$ -dicarboxylic, and the corresponding  $\alpha$ -di- and  $\alpha$ -tri-carboxylic acids. The molecular weights thus determined agree with the accepted constitutions for these substances, but in the case of methyloxalosuccinic and  $\alpha$ -oxalotricarballic esters, the results are abnormally high.

W. O. W.

**Acidic Character of Ethyl Oxalacetate.** LOUIS JACQUES SIMON (*Compt. rend.*, 1910, 150, 1760. Compare Abstr., 1904, i, 648; 1907, i, 963).—The author has already called attention to the acidic character of ethyl oxalacetate recently studied by Gault (preceding abstract).

W. O. W.

**Decomposition of Formaldehyde at a Red Heat.** ARMAND GAUTIER (*Compt. rend.*, 1910, 150, 1725-1726. Compare this vol., ii, 607).—When a mixture of hydrogen and formaldehyde is passed through a porcelain tube heated to redness, the formaldehyde is decomposed in accordance with the equation:  $CH_2O = CO + H_2$ . If passed over iron at  $650^\circ$ , the gaseous product contains in addition 0.8% of methane.

W. O. W.

**Electro-syntheses.** V. SIMA M. LOSANITSCH (*Ber.*, 1910, 43, 1871-1874. Compare this vol., i, 1).—Methylal, when subjected to the silent electric discharge, yields carbon monoxide, methane, hydrogen, a small amount of unsaturated hydrocarbons, and large

quantities of aldehydes, which are polymerides of formaldehyde and acetaldehyde, namely,  $C_8H_{10}O_2$ ,  $C_8H_{12}O_2$ ,  $C_8H_{14}O_2$ , and  $(C_8H_{10}O_2)_n$ .

Acetal yields aldehyde compound:  $C_8H_{12}O_2$ , h. p. 100—110°/16 mm.;  $C_{16}H_{20}O_2$ , h. p. 140—200°/16 mm., and  $C_{14}H_{22}O_2$ .

Methyl sulphide yields the compounds  $C_8H_{12}S_2$ , b. p. 45—50°/14 mm.;  $C_8H_{10}S_2$ , h. p. 80—90°/14 mm.;  $C_8H_{12}S_2$ , h. p. 120—140°/14 mm., and  $C_7H_{14}S_2$ , which are polymerides of formaldehyde and thioacetaldehyde.

Pentane and ammonia yield an oily hydrocarbon,  $C_nH_{2n}$ , and a base,  $C_6H_{13}N$ , which has h. p. 90—95°/14 mm.

Ether and ammonia yield a base,  $C_9H_{17}ON_3$ .

J. J. S.

**Injurious Action of the Sun's Rays on Acetone.** BATIK (*Chem. Zeit.*, 1910, 34, 735).—When acetone is exposed to the direct rays of the sun, it is affected in such a way that it almost immediately decolorises permanganate. When kept overnight, however, it regains its ordinary properties. The direct rays of the sun are necessary for this effect, and their influence is not prevented by the use of coloured, light-absorbing flasks. According to the author the action only takes place in May and June to any extent; it has not been observed in April, August, or September.

T. S. P.

**Photochemical Synthesis of Carbohydrates from Carbon Monoxide and Water Vapour in the Absence of Chlorophyll; Photochemical Synthesis of Quaternary Compounds.** DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, 150, 1690—1693).—Synthetical processes of the type occurring in plants may in some cases be effected by the aid of the quartz-mercury lamp. The following reactions have been studied from this point of view, and carried out through the agency of ultra-violet light:  $CO + O \rightleftharpoons CO_2$ ;  $CO + H_2 \rightleftharpoons H \cdot CHO$ ;  $xCH_2O \rightleftharpoons (CH_2O)_x$ ;  $H_2 + O \rightleftharpoons H_2O$ . Formamide has been obtained by exposing a mixture of carbon monoxide and ammonia to ultra-violet light.

W. O. W.

**Carnine and Inosic Acid. IV.** FRANZ HAISER and FRANZ WENZEL (*Monatsh.*, 1910, 31, 357—361. Compare Abstr., 1909, i, 322, 540).—The pentose obtained from inosine and inosic acid has been regarded previously by the authors as *d*-lyxose, mainly on account of the m. p. of the phenylphenylhydrazone. They have now prepared lyxose from galactonic acid by means of mercuric oxide by Guerbet's method, and find that its phenylphenylhydrazone depresses the m. p. of that of the pentose 40°. The pentose, therefore, has been converted into the *p*-bromophenylhydrazone; this has m. p. 166°, corresponding with that of *l*-ribose-*p* bromophenylhydrazone. The authors agree, therefore, with Levene that the pentose from inosine is *d*-ribose.

C. S.

**Identity of Crystallised Aloinose with *d*-Arabinose.** EUGÈNE LÉGER (*Compt. rend.*, 1910, 150, 1695—1697. Compare this vol., i, 463).—Aloinose is shown to be identical with *d*-arabinose. Inasmuch as barbeloin and isobarbeloin yield the same products on hydrolysis, they would appear to be stereoisomeric glucosides.

W. O. W.

**isoMaltol.** ARNOLD BACKE (*Compt. rend.*, 1910, 151, 78—80).—The name *isomaltol* is suggested for the compound the preparation of which from bread or biscuits has already been described (this vol., i, 226). It is very stable, and forms crystals having the composition  $C_6H_{10}O_5$ ; m. p.  $98^\circ$ . It forms a yellow solution in aqueous sodium carbonate, liberating carbon dioxide. The compound reduces Fehling's solution, and gives the iodoform reaction; the *benzoyl* derivative has m. p.  $99^\circ$ . The crystalline *copper salt*,  $Cu(C_6H_9O_5)_2 \cdot H_2O$ , is much more stable than the corresponding salt of maltol. The *methyl* derivative, obtained by the action of diazomethane, crystallises in tablets, m. p.  $102^\circ$ , subliming in long needles. *isoMaltol* also differs from maltol in not yielding acetic acid on hydrolysis, and in the formation of a yellow, crystalline compound, m. p.  $138^\circ$ , when treated with amyl nitrite. Phenylhydrazine brings about decomposition. The following constitution is suggested for *isomaltol*:  $OH \cdot C \begin{array}{c} \diagup CH-O \\ \diagdown CO \cdot CMe \end{array} = CH$ .

W. O. W.

**Properties of Lintner's Soluble Starch.** E. D. CLARK (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, 7, iv—lvii).—The result of dialysing solutions of soluble starch, precipitating the solution left in the dialyser by means of alcohol and a drop of 10% sodium chloride solution, and examining both the precipitate and the solution leads the author to the conclusion that soluble starch carries associated with it certain amounts of dextrans with reducing properties, and that it can only be partially freed from these by dialysis or precipitation.

Soluble starch of low reducing power can be prepared in a few minutes by the following process: A thick starch paste made by pouring a suspension of 4 grams of potato starch in 15 c.c. of cold water into 200 c.c. of water at  $95^\circ$ , is cooled to  $40^\circ$ , and then mixed with 5 c.c. of filtered saliva and stirred rapidly. In two or three minutes the whole is liquefied, and is then poured into 95% alcohol and a drop of 10% sodium chloride solution added. The soluble starch is filtered quickly, dropped into a little boiling water to destroy ptyalin, and immediately cooled. The substance is readily soluble in water, whereas Lintner's starch is not.

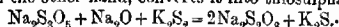
J. J. S.

**Autoxidation of Ethyl Dialkylthiocarbamates.** OTTO BILLETER (*Ber.*, 1910, 43, 1853—1857. Compare Delepine, this vol., i, 295).—Ethyl dimethylthiocarbamate and analogous esters fume and phosphoresce in contact with atmospheric oxygen, giving rise to a characteristic odour, analogous to that formed during the autoxidation of phosphorus. In closed vessels the phenomenon ceases after a short time, and is also inhibited by pressures of 5—10 atmospheres. The action is most pronounced in the presence of alkalis, and neither ozone nor hydrogen peroxide appears to be formed. In open vessels and under favourable conditions, the process continues until all the substance is used up.

The velocity of the absorption of oxygen remains constant until nearly the end of the operation, provided the pressure of the oxygen

is constant and that regular shaking is adopted. Toward the end the rate diminishes rapidly, then increases again, and becomes constant, but with a velocity some 1/100th of the original.

It is probable that the thiocarbamate first forms an unstable peroxide, which decomposes, yielding the carbamate,  $\text{NMe}_2\text{CO}\cdot\text{OEt}$ , and sulphur monoxide, and that the latter reacts with the alkali present, forming a thiosulphate. In most cases more than the theoretical amount of oxygen is absorbed, owing to the formation of sulphite and sulphate, and salts of an acid,  $\text{H}_2\text{S}_2\text{O}_3$ . This acid can be regarded as a mixed anhydride of sulphurous and thiosulphuric acid. The sodium salt,  $\text{Na}_2\text{S}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ , forms definite crystals, and is oxidised by iodine to sodium trithionate:  $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} + \text{I}_2 = \text{Na}_2\text{S}_4\text{O}_6 + 2\text{HI}$ . Potassium disulphide, on the other hand, converts it into thiosulphate:



*Methyl dimethylthiocarbamate*,  $\text{NMe}_2\text{CS}\cdot\text{OMe}$ , is a colourless liquid, b. p.  $68\cdot2^\circ/10$  mm., m. p.  $3\cdot2^\circ$ , and  $D_4^{20}$   $1\cdot0773$ . The *ethyl* ester has b. p.  $82\cdot6^\circ/10$  mm., m. p.  $14\cdot3^\circ$ , and  $D_4^{20}$   $1\cdot0343$ ; the *propyl* ester, b. p.  $96\cdot5\text{--}97\cdot5^\circ/12$  mm., and  $D_4^{20}$   $1\cdot0160$ ; the *isobutyl* ester, m. p.  $28\cdot8^\circ$ , and the *isocamyl* ester,  $\text{NMe}_2\text{CS}\cdot\text{OC}_5\text{H}_{11}$ , b. p.  $119\text{--}119\cdot5^\circ/10$  mm., and  $D_4^{20}$   $0\cdot9688$ .

*Methyl diethylthiocarbamate*,  $\text{NEt}_2\text{CS}\cdot\text{OMe}$ , has b. p.  $105\cdot2\text{--}105\cdot6^\circ/10$  mm., and  $D_4^{20}$   $1\cdot0078$ .

Other sulphur compounds, such as ethyl carbamate, ethyl phenyl-ethylcarbamate, ethyl thiocarbonato, and tetramethylcarbamide, do not appear to be capable of absorbing oxygen.

*Tetramethylthiocarbamide*,  $\text{CS}(\text{NMe}_2)_2$ , forms colourless crystals, m. p.  $73\cdot8^\circ$ . J. J. S.

**New Case of Spontaneous Oxidation with Phosphorescence.** MARCEL DELÉPINE (*Compt. rend.*, 1910, 150, 1607—1608. Compare this vol., i, 295).—The property of spontaneous phosphorescence exhibited by compounds containing the  $\text{S}\cdot\text{C}\cdot\text{O}\cdot$  group is shared by thiocarbonyl chloride. Substances containing the  $\text{O}\cdot\text{CS}\cdot\text{NH}_2$  group, or the  $\cdot\text{S}\cdot\text{C}\cdot\text{O}\cdot$  or  $\cdot\text{S}\cdot\text{C}\cdot\text{O}\cdot$  groupings, are not phosphorescent.

W. O. W.

**Crystallography of the Salts of Methylguanidine.** ARTHUR SCHWANTKE (*Arch. Pharm.*, 1910, 248, 390—397).—The crystallographic examination of the platinichloride and the aurichloride of the methylguanidine obtained by Schenck by the oxidation of  $\gamma$ -methylglycoxyamidine (this vol., i, 546) proves the identity of these salts with the corresponding salts of the methylguanidine obtained by the oxidation of creatine or from methylamine and cyanamide. C. S.

**Synthetical Homocholines.** FERNAND MALENGREAU and A. LEBAILLY (*Zeitsch. physiol. Chem.*, 1910, 67, 35—41).—Several homocholines have been synthesised in order to compare them with neosine, which is also a homologue of choline, according to Kutscher and Ackermann (*Abstr.*, 1908, i, 675).

*$\gamma$ -Homocholine* ( $\gamma$ -hydroxytrimethylpropylammonium chloride),  
 $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{Cl}$

obtained by heating trimethylenedichlorohydrin with a 33% trimethylamine solution at 100° for six hours, forms large, colourless, prismatic crystals, which are deliquescent. The hydroxide forms a syrup, which slowly crystallises. The aurichloride,  $C_6H_{15}ONAuCl_4$ , forms glistening plates, m. p. 183° (corr.), and the platinumchloride,  $(C_6H_{15}ON)_2PtCl_6$ , crystallises from 85% alcohol in characteristic, long, silky, orange-red needles, m. p. 227—228° (corr.). These salts are quite different from those of a  $\gamma$ -homocholine described by Schmidt and Partheil (Abstr., 1892, 950).

$\beta$ -Hydroxytrimethylpropylammonium chloride ( $\beta$ -homocholine),  $OH \cdot CHMe \cdot CH_2 \cdot NMe_3Cl$ , obtained by heating propylene dichlorohydrin,  $CH_2Cl \cdot CHMe \cdot OH$ , with 33% alcoholic trimethylamine solution at 100° for six hours, forms extremely deliquescent crystals. The hydroxide is a syrup, and at 170—180° yields trimethylamine and the glycol. The aurichloride,  $C_6H_{15}ONAuCl_4$ , crystallises in glistening, golden-yellow plates, m. p. 195—196° (corr.). The platinumchloride,  $(C_6H_{15}ON)_2PtCl_6$ , crystallises in orange-yellow, regular octahedra. The two isomeric bases are most readily distinguished by means of their characteristic platinumchlorides.

An isomeric  $\beta$ -homocholine (isopropyleneurine),  $OH \cdot CH_2 \cdot CHMe \cdot NMe_3Cl$ , has been described by Morley (Abstr., 1881, 151). J. J. S.

Glycocyamine and Glycoyamidine. MARTIN SCHENCK (*Arch. Pharm.*, 1910, 248, 376—389).—The derivative obtained by the methylation of glycocyamine, and regarded as  $\delta$ -methylglycocyamine by Korndörfer (Abstr., 1905, i, 29), is proved by oxidation by alkaline 5% potassium permanganate at 50—60° to be  $\gamma$ -methylglycoyamidine,  $NH \cdot C \begin{smallmatrix} \nearrow NH \cdot CH_2 \\ \searrow NMe \cdot CO \end{smallmatrix}$ , since the products are oxalic acid and the same methylguanidine as is obtained by the oxidation of creatinine. A comparative experiment on the oxidation of creatinine by the preceding oxidising mixture shows that, not only methylguanidine, but also guanidine itself is formed. C. S.

Compounds of Amino-acids and Ammonia. VI. PETER BERGELL and THEODOR BRÜSCH (*Zeitsch. physiol. Chem.*, 1910, 67, 97—103. Compare Bergell and Wüllig, this vol., i, 304).—*dl*-Leucinamide is fermented by liver extract, and yields *d*-leucinamide; the same type of reaction is brought about by kidney extract.

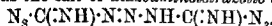
*dl*-Alaninamide also undergoes asymmetric fermentation to a certain extent when left in contact with kidney extract or meat extract.

Löb and Higuchi's placenta powder is without action on leucinamide, whereas placenta magma ferments both leucinamide and alaninamide, and yields the active compounds.

*dl*-Leucinamide gives an onion-red coloration with dilute sodium hydroxide and a drop of very dilute copper sulphate solution; the addition of more copper sulphate produces a violet-red coloration, and with concentrated solutions a heavy precipitate is formed. When dissolved in dilute hydrochloric acid, neutralised with *N*-sodium

hydroxide, filtered, and evaporated under reduced pressure, flat, onion-red prisms are obtained; they melt at  $222-223^{\circ}$  (corr., decomp.), and contain C 29.69, H 8.14, N 17.25, and Cu 19.7%. J. J. S.

**Diazoaminotetrazolic Acid.** KARL A. HOFMANN and HEINRICH HOCK (*Ber.*, 1910, 43, 1866—1871. Compare this vol., i, 232, 446).—Sodium nitrite in the presence of acetic acid reacts in the cold with aminoguanidine dinitrate, yielding a sodium salt,  $C_2H_2N_{11}Na_2 \cdot 2H_2O$ , which is regarded as the salt of *diazoaminotetrazolic acid*,



The acid crystallises in doubly refracting, glistening lamellæ containing  $1H_2O$  after drying under reduced pressure over phosphoric oxide. It is a strong tribasic acid.

The *disodium* salt,  $C_2HN_{11}Na_2 \cdot H_2O$ , crystallises in orange-red prisms, and yields yellow aqueous solutions which are slightly acid. The *barium* salt,  $(C_2N_{11})_2Ba_2 \cdot 8H_2O$ , forms sulphur-yellow plates, which rapidly effloresce. The *ammonio-copper* salt,  $(C_2N_{11})_2Cu \cdot 2NH_3$ , crystallises in dark green, pleochroic plates; when mixed with potassium chlorate and gum, it forms a powerful detonator. The acid and all the salts explode when heated.

The *disilver* salt,  $C_2HN_{11}Ag_2 \cdot H_2O$ , is obtained by washing the precipitated salt with dilute ammonia and then with dilute nitric acid; if the washing with nitric acid is omitted, the *tertiary silver* salt,  $C_2N_{11}Ag_3$ , is obtained.

The acid and its salts are stable towards nitrous acid, but are decomposed by stannous chloride and hydrochloric acid, yielding aminotetrazole and tetrazylhydrazine (Thiele and Marais, *Abstr.*, 1893, i, 441):  $HN_3C \cdot N \cdot N \cdot NH \cdot CN \cdot H + 4H = HN_3C \cdot NH \cdot NH_2 + NH_2 \cdot CN \cdot H$ .

This supports the constitution ascribed to the acid, and further confirmation is obtained by the synthesis of the acid by partial diazotisation of aminotetrazolic acid.

When boiled with acidified water, the sodium salt yields nitrogen and cyanogen, together with aminotetrazole, a decomposition analogous to that of diazoaminotetrazole to aminotetrazole, nitrogen, and cyanogen. With permanganate and dilute sulphuric acid, more than seven atoms of oxygen are taken up by the acid. J. J. S.

**Alkyl Derivatives of Sodium and Their Reactions with Ethers.** PAUL SCHOMIGIN (*Ber.*, 1910, 43, 1931—1938. Compare *Abstr.*, 1907, i, 753; 1908, i, 867, 881).—The reaction between sodium and mercury diethyl takes place in the following stages at  $100-170^{\circ}$ :  $Hg(C_2H_5)_2 + 2Na = Hg + 2C_2H_5Na$ ,  $2C_2H_5Na + 2Hg = 2NaHg + C_2H_4 + C_2H_6$  (compare Buckton, *Annalen*, 1859, 112, 230), as equal volumes of ethylene and ethane are formed during the reaction. Butane is not formed (compare Krafft and Götting, *Ber.*, 1888, 21, 3180). When sodium reacts with mercury diethyl in a solution of light petroleum, ether, or hexane, black, spontaneously inflammable incrustations are formed on the surface of the sodium, and the liquid remains clear; when ether is used as solvent, a voluminous precipitate of sodium ethoxide is formed, according to the equation:  $C_2H_5Na + (C_2H_5)_2O = C_2H_5ONa + C_2H_6 + C_2H_4$ . It is possible that an



active compound,  $\text{OEt}_2\text{Na}$ , is first formed, and that this subsequently decomposes. Other ethers react in a similar manner. Sodium *iso*-xyl (from sodium and mercury di*iso*amyl) and ethyl ether yield sodium ethoxide and not sodium *iso*amyl oxide. Sodium *ethyl* and phenetole yield sodium phenoxide.

J. J. S.

**Secondary Action of Aluminium Chloride on Aromatic Chloro-compounds.** JAMES LAVAUX and MAURICE LOMBARD (*Bull. Soc. chim.*, 1910, [iv], 7, 539—542).—Friedel and Crafts explained the formation of dimethylantracene in the action of benzyl chloride on toluene in presence of aluminium chloride as due to the occurrence of some xyl chloride in the benzyl chloride used, but this explanation is invalid, since if xyl chloride yields dimethylantracene under these conditions, benzyl chloride should yield anthracene, and further it has been shown that benzyl chloride, free from xyl chloride, still furnishes dimethylantracene. Re-investigation of the products formed in this type of reaction indicates that two reactions may occur, represented by the following equations:  $\text{R} \cdot \text{Me} + \text{AlCl}_3 = \text{R} \cdot \text{AlCl}_2 + \text{MeCl}$  and  $\text{R} \cdot \text{CH}_2\text{Cl} + \text{AlCl}_3 = \text{R} \cdot \text{AlCl}_2 + \text{CH}_2\text{Cl}_2$ . The methyl chloride thus formed reacts with aromatic hydrocarbons to form polymethylbenzenes, and the methylene chloride condenses with aromatic hydrocarbons, or in their absence with the aromatic chloro-compounds, to give anthracenes, the latter being always a secondary reaction. In support of these views, the following results of condensations in presence of aluminium chloride are given. Benzyl chloride reacts (1) with benzene to furnish diphenylmethane and anthracene; (2) with toluene to give phenyltolylmethane and a mixture of 1:6- and 2:7-dimethylantracenes. Xyl chloride condenses with toluene to give ditolylmethane and a mixture of 1:6- and 2:7-dimethylantracenes. Benzyl chloride alone condenses to form "benzylene resin,"  $(\text{C}_6\text{H}_5 \cdot \text{CH})_n$ , which on distillation yields some anthracene. Xyl chloride also yields "benzylene resin," but in addition small quantities of the 1:6- and 2:7-dimethylantracenes.

T. A. H.

**Compounds of Trinitrobenzene with Hydrazine, Phenylhydrazine, and Azobenzene: The Side Valency of the Nitro-group.** KARL A. HOFMANN and H. KIRMREUTHER (*Ber.*, 1910, 43, 1764—1767).—Trinitrobenzene forms well-characterised crystalline compounds with hydrazine, phenylhydrazine, and azobenzene, of which the two former are deep red and the third is orange in colour. These are regarded as true molecular compounds, as they are quantitatively decomposed by solvents, for example, water, into their components.

The hydrazine salts of the nitrophenols are lighter and more faintly coloured than trinitrobenzene hydrazine. Trinitro-xylene and trinitromesitylene do not form similar coloured molecular compounds with hydrazine; trinitrotoluene yields a red solution, but the compound with hydrazine could not be obtained crystalline.

*Trinitrobenzene-dihydrazine*,  $\text{C}_6\text{H}_3(\text{NO}_2)_3 \cdot 2\text{NH}_2 \cdot \text{NH}_2$ , forms crystals, m. p. 122—123° (decomp.), which are deep red by transmitted light, but have a metallic green lustre.

*Trinitrobenzene-phenylhydrazine*,  $\text{C}_6\text{H}_3(\text{NO}_2)_3 \cdot \text{N}_2\text{H}_5\text{Ph}$ , forms dark

red, long, flat prisms, which sinter at  $75-80^{\circ}$  and decompose with a slight explosion.

*Dirinitrobenzene azobenzene*,  $[C_6H_5(NO_2)]_2Ph \cdot N_2 \cdot Ph$ , forms orange, four-sided plates, m. p.  $131-132^{\circ}$ , to a red liquid, which explodes when superheated.

E. F. A.

**Hydro-aromatic Substances.** EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1909, 145-147).—This report deals with the nitro-derivatives of *o*-xylene, the synthesis of isophorone and its homologues, and the constitution of Harries and Antoni's "1:1-dimethyl- $\Delta^{2,5}$ -cyclohexadiene."

E. H.

**Two Solid Polymeric Nitroso- $\psi$ -cumenes.** EUGEN BAMBERGER (*Ber.*, 1910, 43, 1842-1849. Compare Cain, *Trans.*, 1908, 93, 683).— $\psi$ -Cumidine, when oxidised at  $0^{\circ}$  to  $5^{\circ}$  with a neutral solution of Caro's reagent, yields a mixture of two solid *nitroso- $\psi$ -cumenes* (5-nitroso-1:2:4-trimethylbenzene,  $NO \cdot C_6H_3Me_3$ ). The crude product is purified by treatment with cold very dilute hydrochloric acid, and then by steam distillation. The colourless crystals are obtained when the hot alcoholic solution is rubbed with a glass rod. If the solution is left without stirring or rubbing, green crystals, mixed with a few colourless crystals, m. p.  $65^{\circ}$ , are obtained. The green compound is metastable, and passes more or less readily into the colourless. The green compound can also be prepared by melting the colourless form and cooling the melt rapidly by means of cold water. It has a bluish-green colour, melts at  $45-46^{\circ}$ , and is much more readily soluble than the colourless modification in most organic solvents.

Other nitroso-derivatives which form green crystals appear to exist in the one form only. The author has not succeeded in preparing Cain's colourless *p*-nitrosoacetanilide (*loc. cit.*). The green form has m. p.  $179.5-180.5^{\circ}$  (corr.).

$\psi$ -Cumylhydroxylamine,  $C_6H_3Me_3 \cdot NH \cdot OH$ , crystallises in glistening, colourless, flat needles, m. p.  $103.5-104^{\circ}$ , and yields 1:2:5-trimethylquinol when left in contact with dilute sulphuric acid for several days (compare *Abstr.*, 1903, i, 557).

J. J. S.

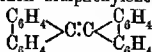
**Isomorphous Sulphonic Derivatives of Benzene.** HENRY A. MIERS, HENRY E. ARMSTRONG, WILLIAM J. POPE, and WILLIAM P. WINNE (*Brit. Assoc. Report*, 1909, 141-143).—This report deals with the crystallographic relationships of *p*-dibromobenzene-sulphonyl chloride and bromide, -sulphonanilide, and ethyl sulphonate, 1-chloro-4-iodobenzene-3-sulphonyl chloride and bromide, and *p*-diiodobenzene-sulphonyl chloride towards each other and towards benzene, with especial reference to the Pope-Barlow theory.

E. H.

**Reaction between Organic Magnesium Compounds and Dibromooanthracene Tetrabromide.** WLADIMIR NAUMOFF (*J. pr. Chem.*, 1910, [ii], 82, 181-182).—Magnesium phenyl, tolyl, mesityl and ethyl bromides react with dibromooanthracene tetrabromide in ethereal solution with the formation of dibromooanthracene, simply withdrawing four atoms of bromine.

T. S. P.

**9:9-Dichlorofluorene and its Conversion into Bidi-phenylene-ethene.** JULIUS SCHMIDT and HANS WAGNER (*Ber.*, 1910, 43, 1796—1802).—Fluorenone, when heated with phosphorus pentachloride, is converted into 9:9-dichlorofluorene, the colour change from glistening yellow,  $>CO$ , to the colourless,  $>CCl_2$ , group being very marked. The chlorine can be eliminated from this compound by means of copper powder, forming first dichloro-*s*-bidiphenylene-ethylene, which is colourless, and then bidiphenylene-ethylene,



(compare Graebe, *Abstr.*, 1896, i, 566), which is intense red. It is conveniently prepared by this reaction. 9:9-Dichlorofluorene reacts with phenylhydrazine, hydroxylamine, etc., similarly to fluorene, and gives the same products, but more readily.

Dichlorofluorene forms colourless quadrants, m. p. 93°, and dissolves in concentrated sulphuric acid with a violet coloration.

Dichloro-*s*-bidiphenylene-ethane,  $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{CCl}:\text{CCl} < \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array}$ , separates in colourless crystals, m. p. 230—232°.

Fluorenone-*p*-nitrophenylhydrazone,  $\begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array} > \text{C}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , prepared either from fluorenone or from dichlorofluorene, crystallises in orange-yellow needles, m. p. 269°. E. F. A.

**Compounds which cause the Red Coloration of Aniline. I. Effect of Oxygen and Ozone, and the Influence of Light in the Presence of Oxygen.** HARRY D. GIBBS (*Philippine J. Sci.*, 1910, 5, 9—16).—Bottles containing aniline are placed in sunlight and constantly agitated for about one month. The stoppers are removed from time to time, and the air over the liquid changed. The deep red liquid is then dissolved in very dilute sulphuric acid; the insoluble portion contains 2:5-dianilinoquinone. Without being filtered, the sulphuric acid solution is extracted with ether. The ethereal extract contains dianilinoquinone, dianilinoquinoneanil, and azobenzene. Another portion of the coloured aniline is poured into 50% acetic acid; when cold, the solution deposits the characteristic twinned crystals of azophenine.

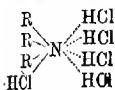
Dry purified aniline, free from sulphur compounds, can be kept unchanged for two months in an atmosphere of an inert gas. In dry, purified oxygen, the coloration of the aniline proceeds slowly in darkness and very rapidly in sunlight. The presence of moisture or impurities is not necessary for the production of the colour. In contact with ozonised oxygen, aniline is instantly coloured, rapidly becomes dark red, and evolves carbon dioxide; ultimately the liquid sets to a crystalline mass of dianilinoquinoneanil. C. S.

**Addition of Hydrogen Chloride to Substituted Anilines at Low Temperatures.** ANTONI VON KORCZYŃSKI (*Ber.*, 1910, 43, 1820—1824. Compare *Abstr.*, 1909, i, 123; Kaufier and Kunz, *ibid.*, 136, 556).—The following compounds have been isolated at

-75°: With 8HCl, *p*-nitrosodimethylaniline; with 6HCl, *p*-nitrosoaniline; with 5HCl, *m*-nitrodimethylaniline; with 4HCl, 2:4-dinitroaniline, 3:5-dinitroaniline, 4:6-dibromo-2-nitroaniline; with  $3\frac{1}{2}$ HCl, 2:6-dinitroaniline; with 3HCl, aniline, diphenylamine, 4:6-dichloro-2-nitroaniline, 2:6-dichloro-4-nitroaniline, 2:6-dibromo-4-nitroaniline, *p*-nitrodimethylaniline, *o*-, *m*-, *p*-aminobenzoic acids; with  $2\frac{1}{2}$ HCl, 2:4-dichloroaniline, dibromo-*o*-toluidine, trichloroaniline; with 2HCl, *p*-toluidine, *o*-, *m*-, *p*-chloroanilines, *o*-, *m*-, *p*-bromoanilines, *p*-iodoaniline, 3:5-dichloroaniline, 3:5-dibromoaniline, dibromo-*p*-toluidine, 3:5-dichloro-2:4:6-tribromoaniline, 4-bromo-2:6-dinitroaniline, carhamide, thiocarbamide; with 1HCl, 6-bromo-2:4-dinitroaniline.

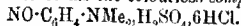
Trinitroaniline does not combine with hydrogen chloride.

The maximum number of molecules of hydrogen chloride is 5, except in the case of the nitroso-derivatives, where the oxygen atom also probably adds on hydrogen chloride. This points to the co-ordinate number 8, and the annexed type of formula is suggested.



It is noticed that monohalogen derivatives of aniline add on 2HCl, and that the introduction of a second halogen atom into the ortho- or para-position can increase the additive capacity of the amine. The introduction of 3 or even 5 halogen atoms does not prevent the formation of hydrochlorides. The introduction of a second nitro-group into the molecule of nitroaniline has much the same effect as the introduction of a second halogen atom into a monohalogen derivative of aniline. Two nitro-groups in the ortho-position with respect to the amino-group are not so favourable to addition as the same groups when in 2:4- or 3:5-positions, and the presence of three nitro-groups can prevent the formation of an additive compound.

The acid sulphate of a base as a rule combines with two molecules of hydrogen chloride less than the base itself; thus *p*-nitrosodimethylaniline sulphate forms the colourless compound,



Naphthaquinoline forms a compound with 5HCl, and its acid sulphate a compound with 3HCl. Quinoline acid sulphate also combines with 3HCl. Ammonium chloride, ammonium sulphate, and hydrazine sulphate do not combine with hydrogen chloride.

Most of the compounds mentioned are colourless, a few have a pale yellow colour, and the compound from nitrosoaniline is yellow.

J. J. S.

**The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives.** FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Report*, 1909, 147—149).—This report [with W. C. EVANS and W. J. JONES] deals with the transformation of *p*-chloroacetylchloroamino-benzene into dichloroacetanilide.

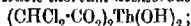
E. H.

**Some New Thorium Salts.** GEORGES KARL (*Ber.*, 1910, 43, 2068—2070).—*Thorium picrate*,  $\text{Th}(\text{C}_6\text{H}_2\text{N}_2\text{O}_7)_4\cdot 10\text{H}_2\text{O}$ , separates as

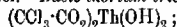
in oil, which solidifies to a yellow, hard, crystalline mass, when ammonium picrate is added to a hot aqueous solution of thorium nitrate. Small, yellow needles, m. p. 52–53°; explodes on heating with the bare flame. It can be dehydrated at 105°, and then forms a vitreous, yellow mass, which is still solid at 100°. At 25°, 100 c.c. of water dissolve 0.3052 gram of the hydrated picrate.

*Thorium hippurate*,  $(\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Th}$ , is formed from thorium nitrate and ammonium hippurate. White, crystalline powder, slightly soluble in water. One hundred c.c. of water dissolve 0.0318 gram at 25°.

*Basic thorium chloroacetates* are obtained when freshly-prepared basic thorium carbonate is added to the various chloroacetic acids. *Basic thorium monochloroacetate*,  $(\text{CH}_2\text{Cl}\cdot\text{CO}_2)_2\text{Th}(\text{OH})_2\cdot\text{H}_2\text{O}$ ; small, white needles from alcohol. *Basic thorium dichloroacetate*,



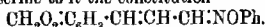
small prisms from alcohol. *Basic thorium trichloroacetate*,



small, shining, and transparent octahedra, which contain water of crystallisation, but effloresce on exposure to the air. T. S. P.

**Behaviour of 3-Nitro-*p*-cresol towards Sulphuric Acid.** II. GUSTAV SCHULTZ and OSKAR LÖW (*Ber.*, 1910, 43, 1899–1902. Compare Abstr., 1909, i, 222).—When 3-nitro-*p*-cresol is added slowly to concentrated sulphuric acid on the water-bath, the product is the same as that obtained by the action of cold fuming sulphuric acid, namely, *β*-acetylacrylic acid. By-products of the reaction are a substance (*α*-nitro-*β*-acetylacrylic acid?), m. p. 206–207° (decomp.), and ammonium 3-nitro-*p*-cresol-5-sulphonate, which is reduced by stannous chloride and hydrochloric acid to the corresponding amino-compound. C. S.

**Action of Nitroso-derivatives on Unsaturated Compounds.** ANGELO ANGELI, LUIGI ALESSANDRI, and RAFFAELLO PRIGNA (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 650–659).—The authors have investigated the action of nitrosobenzene on anethole, isosafrole, safrole, and ethylenegol. In the first two cases no definite reaction-product was isolated. When a mixture of safrole and nitrosobenzene is kept in the dark for four or five days at the ordinary temperature, a substance, crystallising in golden-yellow needles, m. p. 193°, is obtained, in addition to azoxybenzene. The compound has the formula  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$ , and the authors ascribe to it the constitution



It yields nitrosobenzene when exposed to light, or to the action of oxidising agents, and, when it is oxidised with potassium permanganate in alkaline solution, piperic acid is formed. By the action of dilute mineral acids, it is converted into an isomeric compound, which has m. p. 195°, and the authors regard it as a Schiff's base; it is a yellow powder, is soluble in alkalis, and yields a sulphate, m. p. 174°. It forms a benzoyl derivative,  $\text{C}_{20}\text{H}_{15}\text{O}_3\text{N}$ , m. p. 229°, identical with that obtained by the action of benzoyl chloride on *p*-aminophenol. The base is also acted on readily by hydroxylamine, three oximes of the

formula  $C_{10}H_7O_3N$  being produced. The  $\alpha$ -oxime crystallises in long, thin needles, m. p.  $195^\circ$ ; the  $\beta$ -oxime forms lustrous laminae, m. p.  $191^\circ$ , and the  $\gamma$ -oxime, short needles, m. p.  $155^\circ$ . With benzoyl chloride both the  $\beta$ - and  $\gamma$ -oxime yield the same benzoyl derivative,  $C_{17}H_{13}O_4N$ , m. p.  $175^\circ$ . All three compounds show the behaviour of oximes. When they are boiled with dilute acid, piperonylacetaldehyde is formed; this substance is, however, best prepared by the action of amyl nitrite. Whether prepared in this way or from piperonal by the method of Ladenburg and Scholtz, it has m. p.  $84^\circ$ , although these authors gave (Abstr., 1895, i, 42) m. p.  $70^\circ$ . Phenylhydroxylamine reacts with the aldehyde, forming the same compound of m. p.  $193^\circ$  as is obtained from safrole and nitrosobenzene.

The action of nitrosobenzene on ethyleugenol is similar to its action on safrole: a compound,  $C_{18}H_{15}O_3N$ , is formed, which crystallises in small, yellow needles, m. p.  $155^\circ$ .

R. V. S.

**Phenanthrene Series. XXVIII. Bromination and Nitration of 9-Hydroxyphenanthrene.** JULIUS SCHMIDT and OTTO SPORN (*Ber.*, 1910, 43, 1802—1807. Compare Abstr., 1909, i, 134; this vol., i, 312).—By the action of bromine in carbon disulphide solution, 9-hydroxyphenanthrene yields a dibromo-derivative containing one bromine atom in position 3 in the nucleus, since it yields 3-bromophenanthraquinone on oxidation with chromic acid. The other bromine atom is in position 9 or 10, and the compound has the formula  $C_{18}H_7Br \cdot C(OH)$  or  $C_{18}H_7Br \cdot CBr$ . The same compound is obtained on brominating 9-acetoxyphenanthrene, and this method is preferable.

Before nitration of 9-hydroxyphenanthrene, the hydroxyl group has to be protected by acetylation, and certain further precautions must be observed to prevent oxidation. A dinitroacetoxy-compound is obtained containing one nitro-group in position 3, and the other is either 9 or 10; it yields 3-nitrophenanthraquinone on oxidation.

3:9-Dibromo-10-hydroxyphenanthrene has m. p.  $135^\circ$ ; 9-acetoxyphenanthrene has m. p.  $77^\circ$ ; 3:9-dibromo-10-acetoxyphenanthrene, prepared by acetylation of the dibromo-derivative, crystallises in colourless needles, m. p.  $177^\circ$ .

3:9-Dinitro-10-acetoxyphenanthrene is a yellow powder, m. p.  $137$ — $138^\circ$ .

E. F. A.

**Behaviour of Aromatic Disulphides at High Temperatures.** OSCAR HINSBERG (*Ber.*, 1910, 43, 1874—1879).—When the simple aromatic disulphides are heated in a sealed tube at  $240$ — $280^\circ$  they decompose into a mixture of the monosulphide and trisulphide. With more complex disulphides, other disturbing reactions take place, which may completely suppress the simple wandering of the sulphur atom.

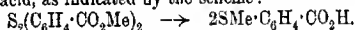
Phenyl disulphide at  $280^\circ$  gives a mixture of monosulphide and trisulphide in the proportions required by the equation:  $2S_2Ph_2 = 3Ph_2 + S_3Ph_2$ .  $\alpha$ -Naphthyl disulphide at  $260$ — $270^\circ$  gives a mixture of the mono- and tri-sulphide. 4:4'-Dithioacetanilide at  $180^\circ$  gives a mixture of the three isomeric dithioacetanilides. At  $240$ — $260^\circ$  a

mixture is obtained, from which it is difficult to separate the constituents; thus far the presence of 4:4'-thioacetanilide has been proved.

Dithiosalicylic acid [*o*-disulphidobenzoic acid,  $S_2(C_6H_4 \cdot CO_2H)_2$ ] at 280° gives a mixture containing the corresponding monosulphide, 2:2'-dicarboxydiphenyl-sulphide (this vol., i, 261), and the thioanhydride of trithiosalicylic [trisulphidobenzoic] acid, which is formed instead of the expected *o*-trisulphidobenzoic acid. The dicarboxy-diphenyl sulphide also loses carbon dioxide to some extent, with the formation of phenyl-2-carboxyphenyl sulphide. *o*-Trisulphidobenzoic

acid thioanhydride,  $CO \cdot C_6H_4 \cdot S_2 \cdot C_6H_4 \cdot CO \cdot S$ , forms light yellow needles, m. p. 75–76°, soluble in chloroform, insoluble in sodium carbonate or cold sodium hydroxide. It slowly dissolves in warm sodium hydroxide, and the addition of hydrochloric acid to the solution precipitates *o*-trisulphidobenzoic acid,  $S_3(C_6H_4 \cdot CO_2H)_2$ , colourless flakes, difficultly soluble in all solvents, m. p. about 300°. In the thioanhydride, the middle ring is a 10-atom one.

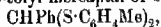
Dimethyl *o*-disulphidobenzoate at 260–280° gives the dimethyl ester of 2:2'-dicarboxydiphenyl sulphide; at the same time a wandering of the methyl group takes place with the formation of *o*-methyl-thiolbenzoic acid, as indicated by the scheme:



T. S. P.

#### Basic Properties of Sulphoxides and their Tautomerism.

EMIL FROMM and G. RAIZISS (*Annalen*, 1910, 374, 90–105).—Sulphides in which the sulphur is combined with a methyl or methylene group combine with halogens, forming dihalogenides; if, however, the sulphur is united directly with aromatic groups on both sides, dihalogenides are not formed. An attempt to ascertain the behaviour towards halogens of a sulphide containing the sulphur united with a  $-CH$  group was unsuccessful; the substance investigated, namely, the *p*-tolyl mercaptal of benzaldehyde,



when acted on by bromine is decomposed with the formation of tolyl disulphide.

Analogously, when a sulphoxide containing a sulphonyl group adjacent to a methyl or methylene group is treated with hydrogen bromide, it yields a dibromide, but if the sulphonyl group is united to two aromatic groups, as in ditolyl sulphoxide,  $SO(C_6H_4Me)_2$ , the sulphoxide is not attacked by hydrogen bromide.

Di-*p*-tolyl dithioethane,  $C_6H_4(S \cdot C_6H_4Me)_2$ , is formed by the interaction of *p*-thiocresol and ethylene bromide in an alcoholic solution of sodium hydroxide; it crystallises in transparent leaflets, m. p. 80°, and when oxidised with nitric acid, chromic acid, or hydrogen peroxide yields the corresponding disulphoxide,  $C_{16}H_{18}O_2S_2$ , which crystallises in silvery, white leaflets, m. p. 166° (decomp.). The following compounds are obtained by suitable methods from the dithio-compound by treatment with chromic acid or nitric acid: *p*-tolylsulphone-*p*-tolylsulpharythane,  $C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot SO \cdot C_6H_4Me$ , long, colourless,

needles, m. p.  $148^{\circ}$ ; *di-p-tolylsulphonethane*,  $C_9H_7(SO_2 \cdot C_6H_5)_2$ , long, glistening, transparent crystals, m. p.  $199-200^{\circ}$ ; *dinitrodi-p-tolylsulphonethane*,  $C_{16}H_{10}O_6N_2S_2$ , long, pale yellow needles, m. p.  $228^{\circ}$ ; *tetranitrodi-p-tolylsulphonethane*,  $C_{16}H_{14}O_{12}N_4S_2$ , yellow leaflets, m. p. above  $300^{\circ}$ .

A solution of di-*p*-tolylidithioethane in chloroform, when treated with bromine at  $0^{\circ}$ , yields the *tetrabromide*,  $C_9H_7(SBr_2 \cdot C_6H_5Me)_2$ , obtained as small, glistening crystals, which appear yellowish-red by transmitted light and dark red by reflected light, m. p.  $68-69^{\circ}$ ; it is so unstable that it cannot be recrystallised, and is decomposed by atmospheric moisture. The tetrabromide is converted by water at  $0^{\circ}$  into the di-*p*-tolylsulphoxyethane just described, and can be regenerated from the latter substance by treatment with hydrogen bromide. On the other hand, di-*p*-tolylsulphoxyethane is converted by bromine in chloroform into the *tetrabromide*,  $C_{16}H_{18}O_2Br_4S_2$ , which crystallises in red prisms, m. p.  $96^{\circ}$ .

*Di-p-tolylidithioethane di-iodide*,  $C_{16}H_{18}I_2S_2$ , is obtained by treating di-*p*-tolylidithioethane (1 part) with iodine (1 part) in hot glacial acetic acid for a short time; it forms steel-blue needles, m. p.  $83^{\circ}$ . The *tetra-iodide*,  $C_{16}H_{18}I_4S_2$ , obtained by using iodine (2 parts) and heating the solution to  $120^{\circ}$  for about three hours, crystallises in wine-red leaflets, m. p.  $88^{\circ}$ .

*Benzyl sulphide dibromide*,  $(CH_2Ph)_2SBr_2$ , is obtained by acting on benzyl sulphide with a solution of bromine in chloroform at  $0^{\circ}$ , or by treating benzyl sulphoxide with hydrogen bromide; it forms yellowish-red crystals, m. p.  $54^{\circ}$ .

The *p-tolylmercaptal* of benzaldehyde,  $C_{21}H_{20}S_2$ , formed by the condensation of benzaldehyde and *p*-thiocresol under the influence of hydrogen chloride, crystallises in long prisms, m. p.  $79^{\circ}$ ; it is oxidised by potassium permanganate, yielding *di-p-tolylsulphonophenylmethane*,  $C_{21}H_{20}O_2S_2$ , which forms stout, pointed plates, m. p.  $163^{\circ}$ .

The *p-tolylmercaptal* of acetone,  $C_{17}H_{20}S_2$ , is similarly prepared; it forms needles, m. p.  $66^{\circ}$ .

W. H. G.

**Active Pinonic and Pinic Acids.** PHILIPPE BARBIER and VICTOR GRIGNARD (*Bull. Soc. chim.*, 1910, [iv], 7, 548-557).—A detailed account of work already published (*Abstr.*, 1908, i, 852), showing that Tiemann's *l*-pinonic acid (*Abstr.*, 1896, i, 308) is not identical with the true *l*-pinonic acid derived from *l*-pinene. It is pointed out further that the isopropylheptanonolide derived from Tiemann's acid is not identical with that obtained from true *l*-pinonic acid, and since the structure of the isopropylheptanonolide does not permit of *cis-trans*-isomerism, it follows that Tiemann's acid cannot be a *cis-trans*-isomeride of true *l*-pinonic acid. It is suggested that Tiemann's acid should be called campholenic acid, and that the acid obtained by the same author by the oxidation of  $\beta$ -campholenic acid should be named  $\beta$ -campholenic acid.

*l*-Pinonic acid, crystallised from water over sulphuric acid, forms large, monoclinic prisms [ $a:b:c=0.5782:1.06216$ ;  $\beta=105^{\circ}$ ]. On treatment with sulphuric acid, it yields 1-isopropylheptanonolide,



$\text{COOMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \begin{matrix} \text{OMe} \cdot \text{C} \cdot \text{O} \\ \text{CH}_2 \cdot \text{CO} \end{matrix}$ , m. p.  $47-48^\circ$ ,  $[\alpha]_D - 57.45^\circ$  in alcohol, which separates in colourless, slender needles by addition of light petroleum to its solution in ether. On oxidation with sodium hypochlorite, *l*-pinonic acid furnished *d*-pinic acid,  $[\alpha]_D + 70.10^\circ$ , and a second substance, which decomposes on distillation and may be a mixture of *cis*- and *trans*-isomerides. *d*-Pinonic acid, obtained by oxidising *d*-pinene from myrtle oil, furnishes *d*-isopropylheptanonolide, m. p.  $47^\circ$ ,  $[\alpha]_D + 57.88^\circ$ , and on oxidation *l*-pinic acid, m. p.  $135^\circ$ , which crystallises in small needles. A fused mixture of equal quantities of the two pinic acids gives *r*-pinic acid, m. p.  $101-102^\circ$ . In the preparation of both *l*- and *d*-pinonic acids some *r*-pinonic acid is also formed.

T. A. H.

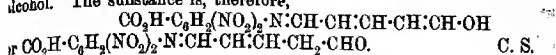
**New Synthesis of Aromatic Carboxylic Acids from Hydrocarbons.** II. PAUL SCHORIGIN (*Ber.*, 1910, 43, 1938—1942. Compare Abstr., 1908, i, 886).—An examination of the gaseous products formed by the action of dry carbon dioxide on a mixture of benzene, sodium wire, and mercury diethyl proves that the reaction proceeds in the stages: (1)  $\text{HgEt}_2 + 2\text{Na} = \text{Hg} + 2\text{NaEt}$ ; (2)  $\text{C}_6\text{H}_6 + \text{C}_2\text{H}_5\text{Na} = \text{C}_6\text{H}_5\text{Na} + \text{C}_2\text{H}_6$ , and (3)  $\text{C}_6\text{H}_5\text{Na} + \text{CO}_2 = \text{C}_6\text{H}_5\text{CO}_2\text{Na}$ , as the proportion of ethane to ethylene is much greater (12:1) than is obtained by the action of sodium on mercury diethyl (this vol., i, 547). Benzoic acid can also be obtained by substituting sodium isocamyl for sodium ethyl, but the yield is not good.

The following acids have been synthesised by the action of carbon dioxide on sodium, mercury diethyl, and the respective hydrocarbon: *o*-Tolylacetic acid and *p*-tolylacetic acid from *o*- and *p*-xylenes, 3:5-dimethylphenylacetic acid from mesitylene, diphenylacetic acid from diphenylmethane, and *p*-homocoumaric acid from *p*-cymene. The yield is poor in each case.

Thiophen-*a*-carboxylic acid is formed from thiophen, and the yield is somewhat better, 7 grams from 50 grams of thiophen. J. J. S.

**Action of Pyridine on 2-Chloro-3:5-dinitrobenzoic Acid.** THEODOR ZINCKE (*J. pr. Chem.*, 1910, [ii], 82, 17—23. Compare this vol., i, 585).—When a mixture of pyridine and 2-chloro-3:5-dinitrobenzoic acid is kept for some hours, and is then heated for a short time on the water-bath, the betaine,  $\begin{matrix} \text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CO} \\ \text{C}_5\text{NH}_5 \text{---} \text{O} \end{matrix}$ , m. p.  $186-188^\circ$  (decomp.), is formed. It separates from water in colourless, rhombic plates, yields 3:5-dinitro-2-anilinobenzoic acid, m. p.  $214^\circ$ , or the corresponding toluidine-derivative, m. p.  $228^\circ$ , by heating with aniline or *p*-toluidine in glacial acetic acid, and the methyl ester, m. p.  $125^\circ$ , or the ethyl ester, m. p.  $97^\circ$ , of dinitrosalicylic acid by treatment with methyl or ethyl alcohol at  $100^\circ$ . The action of 2*N*-sodium hydroxide on an aqueous solution of the betaine, which is subsequently acidified, leads to the formation of a reddish-brown, crystalline substance,  $\text{C}_{12}\text{H}_9\text{O}_7\text{N}_2\text{H}_2\text{O}$ , m. p.  $135-140^\circ$  (decomp.), which regenerates the betaine by heating with hydrogen chloride in glacial acetic acid, yields

3,5-dinitro-2-aminobenzoic acid by treatment with boiling glacial acid and concentrated hydrochloric acids, and forms the dianilide,  $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHPh}$  (Abstr., 1904, i, 921), and dinitro-aminobenzoic acid when boiled with an excess of aniline and a little alcohol. The substance is, therefore,



**Lactonoid Anhydrides of Acylated Amino-acids. IV.** Behaviour of Hippuric Acid, Hippuramide, and *r*-Acetylalanine towards Dehydrating Agents. ERNST MOHR and FR. FROSCHMANN (*J. pr. Chem.*, 1910, [ii], 82, 60—64).—A continuation of the preceding paper (this vol., i, 483). Attempts to prepare the lactonoid anhydride of hippuric acid by heating the acid with acetic anhydride have been unsuccessful, as also have been experiments on the formation of a cyclic imide by heating hippuramide with *N*-sodium stearoxide or with acetic anhydride. Also, the heating of *r*-acetylalanine and acetic anhydride does not yield a product from which the lactone can be isolated. C. S.

**General Reaction for the Conversion of Saturated Fatty Acids,  $\text{CH}_3\text{R}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , into Ketones,  $\text{R}\cdot\text{CO}\cdot\text{CH}_2$ .** HENRY J. DAKIN (*Am. J. Chem. J.*, 1910, 44, 41—48).—The generality of the reaction whereby the sodium or ammonium salts of fatty acids are converted into ketones to the extent of 5—10% by excess of 3% hydrogen peroxide (Abstr., 1908, i, 74, 119; ii, 720) has been tested, in addition to the cases already recorded, it is found that phenylacetic acid yields benzaldehyde, and phenylbutyric acid a volatile ketone with the odour of benzyl methyl ketone. C. S.

**New Method of Alkylation with Benzyl Cyanide.** Alkylation of Nitriles of the Formula  $\text{CHPhR}\cdot\text{CN}$ . F. BODROUX and ELIX TABOURY (*Bull. Soc. chim.*, 1910, [iv], 7, 666—670, 670—672).—An extended account of work already dealt with (this vol., i, 257, 382), fuller details of the method of working being given. The following new data are recorded.

*a*-Phenyl- $\beta$ -methylbutyric acid, m. p. 61—62°, obtained by boiling the corresponding nitrile (*loc. cit.*) during thirty-six hours with potassium hydroxide in alcohol, or during six hours if amyl alcohol is used as solvent, crystallises in colourless prisms.

*a*-Phenyl- $\alpha$ -ethylbutyramide, m. p. 52°, obtained by hydrolysis of the nitrile (*loc. cit.*), forms colourless prisms, as does also *a*-phenyl- $\gamma$ -methyl-propylvaleramide,  $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHPr}\cdot\text{Ph}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 84—85°.

T. A. H.

**1-Acetyl-1-methylcyclohexane.** P. JOSEPH TABOURIECH (*Compt. rend.*, 1910, 150, 1606—1607. Compare Abstr., 1909, i, 796).—Oxidation of the ketone obtained by the action of acids on cyclohexanolpropan- $\beta$ -ol leads to the formation of the ketonic acid,  $\frac{1}{2}\text{H}_{10}\text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , b. p. 141°/20 mm. This forms a semicarbazone, m. p. 198°, and a semicarbazone methyl ester, m. p. 158°; the oxime

decomposes at  $160^{\circ}$ , losing water and carbon monoxide, and forming the nitrile,  $C_6H_{10}CN$ , b. p.  $180^{\circ}$ , which, on hydrolysis, furnishes an acid identical with Zelinski's 1-methylcyclohexane-1-carboxylic acid (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 477). The original ketone, therefore, is 1-acetyl-1-methylcyclohexane,  $C_6H_{10}MeCOMe$ . W. O. W.

**$\alpha$ -Amino-*p*-hydroxyphenylacetic Acid.** JULES ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1910, [iv], 7, 516—518).—The first part of an investigation of the homologues of tyrosine, which are likely to be of biological interest. The preparation and properties of  $\alpha$ -amino-*p*-hydroxyphenylacetic acid, the next lower homologue, are described. The acid was prepared by the action of potassium cyanide and ammonium chloride on anisaldehyde, the resulting aminonitrile being hydrolysed and the acid obtained demethylated by Zeisel's method.

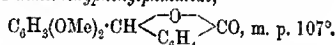
$\alpha$ -Amino-*p*-methoxyphenylacetonitrile,  $OMe \cdot C_6H_4 \cdot CH(NH_2)CN$ , m. p.  $65^{\circ}$ , is unstable, and evolves hydrogen cyanide at atmospheric temperatures; the hydrochloride is crystalline. The corresponding acid already prepared by Tiemann and Köhler (*Abstr.*, 1882, 57) yields a crystalline hydrochloride, and on demethylation gives  $\alpha$ -amino-*p*-hydroxyphenylacetic acid, which crystallises in long, colourless prisms, and yields crystalline salts with halogen acids and a pale blue, crystalline copper derivative. Chlorine water and bromine water give precipitates; the bromo-compound so formed has m. p.  $90^{\circ}$ . The acid may be characterised by its copper derivative, the red colour produced by Millon's reagent, the blue tint furnished by alkaline hypochlorites, and the fact that tyrosinase produces no change in colour. The last two tests serve to distinguish this acid from tyrosine. T. A. H.

**Reduction and Derivatives of *o*-Nitrocinnamoylformic Acid.** GUSTAV HELLER (*Ber.*, 1910, 43, 1923—1927).—[With EDMUND WEIDNER]—*o*-Nitrocinnamoylformic acid forms an ethyl ester, m. p.  $71^{\circ}$ , which separates from alcohol in golden-yellow needles, an oxime, m. p.  $157^{\circ}$ , and *cis*- and *trans*-modifications of the phenylhydrazide. The *cis*-form, obtained from the acid and phenylhydrazine in alcohol at  $0^{\circ}$ , is precipitated from acetone solution by petroleum in tufts of faintly yellow needles, responds to Bulow's hydrazide reaction, easily and smoothly yields indigotin by treatment with alkaline water, and is converted at  $100^{\circ}$  or by recrystallisation from 50% acetic acid into the *trans*-isomeride, m. p.  $222^{\circ}$  (decomp.), which is produced directly by treating a hot solution of the acid in 50% acetic acid with phenylhydrazine. The *trans*-modification gives Bulow's reaction, but does not yield indigotin with alkaline water. *o*-Nitrocinnamoylformic acid in ethereal solution is reduced by aqueous ferrous sulphate and ammonium hydroxide to 4-keto-1:4-dihydroquinoline-2-carboxylic acid. C. S.

**Complete Methylation with Methyl Sulphate.** JOSEF TAMBOUR (*Ber.*, 1910, 43, 1882—1889).—Waliaschko's extension (*Abstr.*, 1909, i, 248) of Preker and Kostanecki's generalisation (*Abstr.*, 1893, i, 217) has been supported by the author's experiments, which show that the following fully methylated compounds can be obtained by submitting the partially methylated substances to the repeated energetic action of

methyl sulphate and alkali. 1-Methoxyxanthone from 1-hydroxyxanthone; 2-methoxy-4-ethoxyacetophenone, m. p. 49°, from resacetophenone ethyl ether; 4-methoxy-2-ethoxyacetophenone, m. p. 7°, from resacetophenone methyl ether and ethyl sulphate; resacetophenone dimethyl ether, m. p. 44°, from the monomethyl ether; 2-hydroxy-4-methoxydeoxybenzoin, m. p. 90°, from 2:4-dihydroxydeoxybenzoin, and by a repetition of the process, 2:4-dimethoxydeoxybenzoin, m. p. 56°.

[With A. SCHÜRCH]—*Methyl 2'-hydroxy-4'-methoxy-2-benzoylbenzoate*,  $\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ , m. p. 103°, and the corresponding acid are both obtained when ethyl resorcinolphthalein is heated for twelve hours with methyl iodide (2 mols.) and alcoholic potassium hydroxide (2 mols.). Ethylation of resorcinolphthalein in a similar manner yields *2'-hydroxy-4'-ethoxy-2-benzoylbenzoic acid*, m. p. 173°, and its ethyl ester, m. p. 78°. Reduction of 2'-hydroxy-4'-methoxy-2-benzoylbenzoic acid by zinc dust and alcoholic potassium hydroxide leads to the formation of *2'-hydroxy-4'-methoxy-2-benzoylbenzoic acid*, m. p. 140°, a hot alcoholic solution of which with methyl sulphate (3 mols.) and potassium hydroxide (3 mols.) forms the potassium salt of 2':4'-dimethoxy-2-benzoylbenzoic acid, m. p. 149°; the acid in carbon disulphide is converted by phosphorus pentachloride into the corresponding acid chloride, m. p. 166°. Resorcinolphthalein is easily and completely methylated by methyl sulphate (3 mols.) and potassium hydroxide (3 mols.), yielding *methyl 2':4'-dimethoxy-2-benzoylbenzoate*, m. p. 100°. 2':4'-Dimethoxy-2-benzoylbenzoic acid is reduced by zinc dust and alkali to the 2:4-dimethoxyphenylphthalide,



$\beta$ -Resorecylic acid, methyl sulphate, and sodium hydroxide yield, according to the experimental conditions, either *p*-methoxysalicylic acid or  $\beta$ -resorecylic acid dimethyl ether. The chloride of the latter and phloroglucinol trimethyl ether condense in the presence of aluminium chloride to form 2:4:6:2':4'-pentamethoxybenzophenone, m. p. 138°, which is reduced by zinc and alcoholic alkali to 2:4:6:2':4'-pentamethoxybenzhydrol, m. p. 104°. 2:4:2':4'-Tetramethoxybenzophenone has m. p. 130°. 3:4:2':4'-Tetramethoxybenzophenone, m. p. 124°, separates from concentrated alcoholic solution in yellow, prismatic needles, and from dilute solution in small, white leaflets. 2':4:4'-Trimethoxybenzophenone has m. p. 73–74°. C. S.

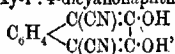
Researches in Benzidine Formation. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 677–683).—A résumé of information already published, in part, in *Ahstr.*, 1905, i, 651; 1909, i, 747. The following new data are given. 2:2'-Dinitrodiphenylmethane-4:4'-dicarboxylic acid, when purified through the ethyl ester, has m. p. 296°, and dissolves in excess of alkali, forming a violet-coloured solution. On reduction with stannous chloride and hydrochloric acid in alcohol, the ethyl ester yields ethyl 2:2'-diaminodiphenylmethane-4:4'-dicarboxylate, m. p. 150° (compare *Ahstr.*, 1905, i, 651), whilst reduction with zinc dust and ammonium chloride, followed by oxidation by means of a current of air in presence of potassium hydroxide,

furnishes 2:2'-azoxydiphenylmethane-4:4'-dicarboxylic acid (Abstr., 1909, i, 747). The ethyl ester of this acid, m. p. 224°, crystallises in bright yellow needles, and on reduction with zinc dust and acetic acid yields ethyl 2:2'-hydrazodiphenylmethane-4:4'-dicarboxylate, m. p. 165°, which crystallises in colourless needles, and on oxidation with yellow mercuric oxide gives ethyl 2:2'-azodiphenylmethane-4:4'-dicarboxylate (loc. cit.).

T. A. H.

**Condensation of Ethyl Oxalate with *o*- and *p*-Xylylene Cyanides.** WILHELM WISLIZENUS and OTTO PENNDORF (*Ber.*, 1910, 43, 1837—1842. Compare Hinsberg, this vol., i, 486).—The small yields of xylylene cyanides obtained by the action of an aqueous-alcoholic potassium cyanide solution on the bromides are due to the formation of xylylene diethyl ethers. A theoretical yield of the *p*-ether,  $C_{12}H_{18}O_2$ , can be obtained by the action of an alcoholic solution of potassium ethoxide on *p*-xylylene bromide. It is a colourless liquid, b. p. 251—252°/734 mm., with a pleasing odour, and when boiled with concentrated hydrochloric acid yields *p*-xylylene chloride.

An 80% yield of *o*-xylylene cyanide can be obtained if suitable precautions are taken. A benzene solution of this cyanide condenses with ethyl oxalate in the presence of sodium ethoxide, yielding Hinsberg's 2:3-dihydroxy-1:4-dicyanonaphthalene,



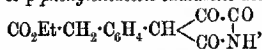
which crystallises in colourless needles, containing  $1H_2O$ , m. p. 278—279°; when anhydrous the compound has m. p. 290—291° (decomp.). With only a small amount of ferric chloride, it gives a reddish-violet coloration, but with a larger quantity of the ferric salt a deep blue colour (compare Hinsberg).

*p*-Xylylene cyanide also condenses with ethyl oxalate, yielding ethyl  $\alpha$ -dicyano-*p*-tolylpyruvate,  $CN \cdot CH_2 \cdot C_6H_4 \cdot CH(CN) \cdot CO \cdot CO_2Et$ , which crystallises in glistening, colourless, flat needles, m. p. 135—136°. It gives a blackish-green coloration with ferric chloride, and a brown copper derivative. When benzoylated in pyridine solution it yields a benzoyl derivative,  $C_{12}H_{16}O_4N_2$ , m. p. 99—101°.

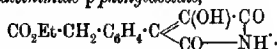
With alcoholic potassium hydroxide it yields potassium oxalate and *p*-xylylene cyanide.

When boiled for ten hours with 25% sulphuric acid it yields *p*-phenyleneaceticpyruvic acid,  $CO_2H \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO \cdot CO_2H$ , m. p. 199—200°.

When the ester is hydrolysed by saturating with hydrogen chloride a solution in ethyl alcohol to which the theoretical amount of water has been added, a product,  $C_{14}H_{18}O_4N$ , m. p. 180—181°, is obtained. This is either the imide of *p*-phenyleneacetic oxalacetic acid,



or ethyl hydroxymaleinimide-*p*-phenylacetate,



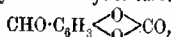
Its solutions in alkalis have a deep yellow colour, and it yields a red

sodium salt. Ethyl cyanophenylpyruvate, when hydrolysed in a similar manner, yields hydroxyphenylmaleinimide (Volhard and Henke, Abstr., 1895, i, 103). J. J. S.

Action of Light on Benzaldehyde in the Presence of Iodine. LUIGI MASCIARELLI and N. BOSINELLI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 562—563).—The oil of b. p. 189—191°/18 mm., which is one of the products of this reaction, and which was formerly described (this vol., i, 389) as a dimeric form of benzaldehyde, has been further investigated, and has proved to be benzyl benzoate. It has b. p. 315—320°, is but slightly volatile in steam, and is quantitatively saponified when boiled with alcoholic potassium hydroxide.

R. V. S.

2:3-Dihydroxybenzaldehyde; *o*-Protocatechuic Aldehyde. HERMANN PAULY and KARL LOCKEMANN (*Ber.*, 1910, 43, 1813—1814. Compare Nötting, this vol., i, 176).—2:3-Dihydroxybenzaldehyde,  $\text{CHO}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , prepared by heating *o*-vanillin with glacial acetic acid and concentrated aqueous hydrobromic acid, crystallises in sulphur-yellow needles, m. p. 108°, and b. p. 235°. Its solution in water has a green colour, and in alkalis an orange-red colour. Its barium salt with carbonyl chloride yields the cyclic carbonate,



in the form of colourless crystals, m. p. 105°, and when this is boiled with methyl alcohol a methyl ester, m. p. 115°, is obtained.

The phenylhydrazones, m. p. 176°, and the semicarbazone, m. p. 226°, are colourless, whereas the Schiff's bases are intensely coloured, although the corresponding compounds derived from other dihydroxybenzaldehydes are colourless. The anil is bright scarlet with a bluish tinge, so also are the derivatives with  $\beta$ -naphthylamine and benzidine. J. J. S.

Transformation of Non-cyclic Diketones into Cyclic Compounds. EDMOND E. BLAISE and A. KOEHLER (*Bull. Soc. chim.*, 1910, [iv], 7, 655—661).—Published already for the most part in Abstr., 1909, i, 287; and this vol., i, 463. The following additional facts are given. 2-Acetyl-1-methyl- $\Delta^4$ -cyclopentene, b. p. 66—68°/9 mm., or 188—189°/755 mm. (compare Perkin and Marshall, Trans., 1890, 57, 241), yields a semicarbazone, m. p. 180°, and on oxidation with permanganate furnishes acetic and  $\gamma$ -acetyl-*n*-butyric acids.  $\gamma$ -Propionyl-*n*-butyric acid yields a semicarbazone, m. p. 196°, and a *p*-nitrophenylhydrazone, m. p. 123°, which forms microscopic crystals. T. A. H.

Condensation of Aldehydes with Methyl Nonyl Ketone,  $\alpha$ -Naphthyl Methyl Ketone and *p*-Methoxyacetophenone, and the Formation of Pyridine Derivatives from the Condensation Products. MAX. SCHOLTZ and W. MEYER (*Ber.*, 1910, 43, 1861—1866. Compare Abstr., 1895, i, 563; 1899, i, 717; 1903, i, 456).— $\alpha$ -Benzylidenemethyl nonyl ketone [styryl nonyl ketone],  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_9\text{H}_{19}$ , has been prepared by Carette (Abstr., 1901, i, 13).

The semicarbazone,  $C_{18}H_{22}ON_3$ , crystallises in yellow needles, m. p.  $121^\circ$ . The isomeric  $\gamma$ -benzylidene derivative, obtained by condensing benzaldehyde with methyl nonyl ketone in the presence of hydrogen chloride (Goldschmidt and Krezmar, Abstr., 1902, i, 40; Harries and Müller, *ibid.*, 1902, i, 295), forms a hydrochloride,  $C_{18}H_{27}OCl$ , which crystallises in snow-white needles, m. p.  $77^\circ$ . The ketone,  $CH_3 \cdot CO \cdot C(\text{CHPh}) \cdot C_8H_{17}$ , is an oil, and yields a semicarbazone,  $C_{19}H_{25}ON_3$ , in the form of glistening plates, m. p.  $130^\circ$ .

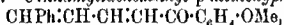
$\alpha$ -Cinnamylidenemethyl nonyl ketone,  $CHPh \cdot CH \cdot CH \cdot CH \cdot CO \cdot C_9H_{19}$ , crystallises in glistening, yellow plates, m. p.  $83^\circ$ . The semicarbazone,  $C_{21}H_{29}ON_3$ , forms pale yellow needles, m. p.  $154^\circ$ , and the oxime,  $C_{20}H_{27}ON$ , yellow, felted needles, m. p.  $89^\circ$ . When distilled, the oxime yields 6-phenyl-2-nonylpyridine,  $C_{20}H_{27}N$ , which is a pale yellow oil, b. p.  $165-170/30$  mm.; the platinumchloride ( $C_{20}H_{27}N$ ) $_2 \cdot H_2PtCl_6$  crystallises in pale red needles, m. p.  $201^\circ$ .

$\alpha$ -Piperonylidenemethyl nonyl ketone,  $CH_2O_2 \cdot C_6H_8 \cdot CH \cdot CH \cdot CO \cdot C_9H_{19}$ , crystallises in pale yellow, felted needles, m. p.  $56^\circ$ ; semicarbazone,  $C_{20}H_{29}O_2N_3$ , forms colourless needles, m. p.  $151^\circ$ . p-Methylstyryl nonyl ketone,  $C_6H_4Me \cdot CH \cdot CH \cdot CO \cdot C_9H_{19}$ , crystallises in plates, m. p.  $123^\circ$ . p-Methoxystyryl nonyl ketone,  $OMe \cdot C_6H_4 \cdot CH \cdot CH \cdot CO \cdot C_9H_{19}$ , forms colourless, glistening plates, m. p.  $63^\circ$ , and yields a semicarbazone,  $C_{20}H_{29}O_2N_3$ , in the form of pale yellow needles, m. p.  $114^\circ$ . p-Propylstyryl nonyl ketone,  $C_3H_7 \cdot C_6H_4 \cdot CH \cdot CH \cdot CO \cdot C_9H_{19}$ , forms soft, colourless needles, m. p.  $144^\circ$ .

The semicarbazone of  $\alpha$ -naphthyl methyl ketone,  $C_{18}H_{19}ON_3$ , forms colourless crystals, m. p.  $205^\circ$ . Cinnamylidenemethyl  $\alpha$ -naphthyl ketone,  $CHPh \cdot CH \cdot CH \cdot CH \cdot CO \cdot C_{10}H_7$ , is an oil; the oxime,  $C_{21}H_{19}ON$ , crystallises in yellow needles, m. p.  $123^\circ$ , and, when distilled, yields a small amount of 6-phenyl-2- $\alpha$ -naphthylpyridine,  $C_{21}H_{15}N$ , as a pale yellow oil, b. p.  $190-192/12$  mm., but the platinumchloride of which crystallises in pale red needles, m. p.  $109^\circ$ .

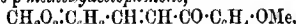
p-Nitrostyryl  $\alpha$ -naphthyl ketone,  $NO_2 \cdot C_6H_4 \cdot CH \cdot CH \cdot CO \cdot C_{10}H_7$ , forms yellow needles, m. p.  $131^\circ$ .

The semicarbazone of p-acetylanisole,  $C_{19}H_{19}O_2N_3$ , forms colourless plates, m. p.  $198^\circ$ . Cinnamylidenemethyl p-methoxyphenyl ketone,



crystallises in yellow, felted needles, m. p.  $93^\circ$ ; its semicarbazone,  $C_{19}H_{19}O_2N_3$ , has m. p.  $189^\circ$ , and its oxime,  $C_{18}H_{17}O_2N$ , forms yellow needles, m. p.  $147^\circ$ , and, when distilled, yields 2-phenyl-6-anisylpyridine,  $C_{18}H_{15}ON$ , as pale yellow needles, m. p.  $119^\circ$ .

Piperonylidene-p-methoxyacetophenone,



forms pale yellow, glistening needles, m. p.  $129^\circ$ , and cinnamylidenemethyl benzyl ketone,  $CHPh \cdot CH \cdot CH \cdot CH \cdot CO \cdot CH_2Ph$ , similar needles, m. p.  $119^\circ$ . J. J. S.

The Friedel-Crafts' Reaction with Chlorides of Unsaturated Acids. ELMER P. KOHLER, GERTRUDE L. HERITAGE, and M. C. BURNLEY (*Amer. Chem. J.*, 1910, 44, 60-76. Compare Abstr., 1907, i, 1050; 1909, i, 938).—Cinnamoyl chloride and excess of benzene in carbon disulphide react with aluminium chloride to form  $\beta\beta$ -diphenyl-

propionophenone, 3-keto-1-phenyl-2:3-dihydroindene, and  $\beta$ -chloro- $\beta$ -phenylpropionophenone; styryl phenyl ketone cannot be isolated. Under similar conditions, cinnamoyl chloride reacts with bromobenzene to form about 25% of *p*-bromophenyl styryl ketone,  $\text{C}_6\text{H}_4(\text{Br})\text{CH}=\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , m. p. 100—101°, and 6-bromo-3-keto-1-phenyl-2:3-dihydroindene,  $\text{C}_6\text{H}_4(\text{Br})\text{CH}(\text{C}_6\text{H}_5)\text{CH}=\text{CH}\cdot\text{CO}$ , m. p. 60—61°, in 30—35% yield. With anisole or phenetole, cinnamoyl chloride yields only the expected unsaturated ketones.

$\alpha\beta$ -Dibromo- $\beta$ -phenylpropionyl chloride is conveniently prepared by adding phosphorus pentachloride to a suspension of dibromocinnamic acid in phosphoryl chloride, removing the chlorides of phosphorus at 150—160° under diminished pressure, and crystallising the residue from carbon disulphide and petroleum. In carbon disulphide cooled by a freezing mixture, the chloride reacts with aluminium chloride alone, hydrogen bromide and a little chloride being evolved, and phenylacetylene, bromostyrene, *p*-bromocinnamic acid, cinnamic acid,  $\alpha$ -bromocinnamic acid, and a small quantity of other unidentified products being formed.

$\alpha\beta$ -Dibromo- $\beta$ -phenylpropionyl chloride, benzene, and aluminium chloride react in carbon disulphide at -20° to form a substance, m. p. 89—90°, which is not dibromophenylpropionophenone, as stated by Collet, but 2-bromo-3-keto-1-phenyl-2:3-dihydroindene, the *semicarbazone* of which as m. p. 212° (decomp.). With bromobenzene, dibromophenylpropionyl chloride yields, in addition to a large quantity of acid by-products due to the reaction between the acid chloride and the aluminium chloride, 2:6-dibromo-3-keto-1-phenyl-2:3-dihydroindene, m. p. 143—144°, and an isomeric substance, m. p. 86°, which is probably a stereoisomeride, since both substances yield *p*-bromo-*o*-benzoylbenzoic acid, m. p. 174°, by oxidation by potassium permanganate in acetone, and the substance of higher m. p. is converted almost quantitatively into the other at its m. p. C. S.

**Acetylenic Ketones.** ÉMILE ANDRÉ (*Compt. rend.*, 1910, 151, 75—78).—In the preparation of acetylenic ketones from the sodium derivatives of unsaturated hydrocarbons, better yields are obtained by using an acid bromide instead of the acid chloride. *iso*Valerylphenylacetylene,  $\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot\text{CO}\cdot\text{CH}_2\text{Pr}^a$ , has b. p. 149—151°/12 mm.,  $D_{20}^{20}$  0.969,  $n_D^{20}$  1.5405. *Hexoylphenylacetylene*,  $\text{C}_6\text{H}_{11}\cdot\text{CO}\cdot\text{C}\equiv\text{CPh}$ , m. p. 14—15°, b. p. 170—172°/12 mm.,  $D_{20}^{20}$  0.965,  $n_D^{20}$  1.5352, was prepared from *hexyl bromide*, b. p. 175—176°. The ketones have also been prepared by oxidising the corresponding secondary alcohols (Moureau, *Abstr.*, 1902, i, 289) with chromic acid in acetic acid solution (compare Dupont, this vol., i, 456). The molecular refractions for five ketonic derivatives of phenylacetylene have been determined, and found to exceed the calculated values by about three units. W. O. W.

**Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane.** VI. Ketochlorides of Dianisylideneacetone [Dip-methoxystyryl Ketone] and Dicinnamylideneacetone. FRITZ STRAUS [with GEORG LUTZ and WERNER HÖSSY] (*Annalen*, 1910, 374, 40—90. Compare this vol., i, 119).—In the main, an amplifica-



tion and extension of the investigations of Straus and Ecker (compare Abstr., 1906, i, 859). Di-*p*-methoxystyryl ketone forms *additive* compounds with the following substances: mercuric chloride, deep yellow, slender, soft needles; calcium chloride, bright yellow powder; phosphoryl chloride, dark reddish-brown oil. The ketone, when treated with phosphorus pentachloride in carbon disulphide, yields the *additive* product,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CCl}_2\cdot\text{PCl}_5$ , a green, crystalline powder, an ethereal solution of which when treated with ice-water and subsequently with sodium hydrogen carbonate and light petroleum yields the *hydrochloride* of  $\beta\beta$ -dichloro- $\alpha\gamma$ -dianisylidenepropene,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CCl}_2\cdot\text{HCl}$ , a dark green powder with a metallic reflex; the ketochloride is obtained from the hydrochloride by boiling with dry petroleum ether, and crystallises in faintly yellow, silvery leaflets, m. p. 91—92° (compare Staudinger, Abstr., 1909, i, 906).  $\beta\beta$ -Dichloro- $\alpha\gamma$ -dianisylidenepropene is converted by water into the *chlorocarinol*,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CCl}\cdot\text{OH}(\text{?})$ , an unstable oil. *Additive* compounds of the ketochloride with the following substances have been prepared: mercuric chloride,  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{Cl}_2\cdot 4\text{HgCl}_2$ , violet crystals with a green reflex; thionyl chloride,  $\text{C}_{19}\text{H}_{18}\text{O}_2\text{Cl}_2\cdot\text{SOCl}_2$ , green powder; phosphoryl chloride, intensely green oil; carbonyl chloride, unstable, green powder; sulphur dioxide,  $3\text{C}_{19}\text{H}_{18}\text{O}_2\text{Cl}_2\cdot 2\text{SO}_2$ , a stable, green, crystalline powder; acetonitrile, propionitrile, benzonitrile, and benzyl cyanide, substances soluble in excess to pale blue solutions. The *sulphate*,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CCl}\cdot\text{OSO}_3\text{H}_2\cdot x\text{H}_2\text{SO}_4$ , prepared by adding sulphuric acid to a solution of the ketochloride in methyl sulphate, crystallises in glistening, green leaflets. The ketochloride is converted by chlorine into the dichloride, m. p. 107—108° (compare Straus and Ecker, *loc. cit.*), which is slowly attacked by a solution of chlorine in tetrachloromethane, but apparently not by bromine in chloroform. The ketochloride or its dichloride, when acted on by methyl alcohol, yields the *methyl ether*,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CCl}\cdot\text{OMe}$ , of the corresponding chloro-carbinol, which crystallises in tufts of white needles or leaflets, m. p. 87—88°, and dissolves in concentrated sulphuric acid or liquid sulphur dioxide, forming blue solutions. Hydrogen chloride converts the methyl ether, dissolved in light petroleum, into the hydrochloride of the corresponding ketochloride, but when the solvent is benzene or carbon disulphide, the ether is converted into the hydrochloride of the corresponding ketone. The action of methyl alcohol on the ketochloride dichloride leads to the formation of two *methyl ethers* having the composition  $\text{C}_{30}\text{H}_{21}\text{O}_2\text{Cl}_2$ , which are probably *cis*- and *trans*-isomerides; the one crystallises in slender, white leaflets, m. p. 99—100°, whilst the other forms colourless needles, m. p. 80—81°; both isomerides are decomposed slowly by methyl alcohol with the elimination of chlorine, and when acted on by active aluminium in an alcoholic solution of sodium methoxide yield the methyl ether of 4:4'-dimethoxydianisyl-.

chlorocarbinal. The ketochloride dichloride, when treated with silver oxide, yields the *dichloride* of the chlorocarbinal,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CHCl} \cdot \text{CHCl} \cdot \text{CCl}(\text{OH}) \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , which crystallises in felted, slender, white needles, m. p. 131°.

Dicinnamylideneacetone, when acted on by phosphorus pentachloride under suitable conditions, yields the corresponding *ketochloride*,  $(\text{CHPh} : \text{CH} : \text{CH} : \text{CH})_2\text{CCl}_2$ , which forms colourless crystals, m. p. 114.5°, and when treated with chlorine in tetrachloromethane yields the *tetrachloride*,

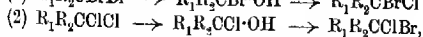
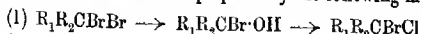
$\text{CHPh} : \text{CH} : \text{CH} : \text{CH} : \text{CCl}_2 \cdot \text{CHCl} \cdot \text{CHCl} \cdot \text{CHCl} \cdot \text{CHPhCl}$ ,

which is also obtained by boiling the ketone dissolved in a mixture of benzene and chloroform with phosphorus pentachloride, and forms colourless, compact crystals, m. p. 172° (decomp.). The tetrachloride combines with further quantities of chlorine, forming mixtures of *hexa-* and *octa-chlorides*. The ketochloride also combines with bromine, yielding a *hexabromide*,  $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{Br}_6$ , which crystallises in tufts of small, colourless prisms decomposing at 219°. The ketochloride forms *additive* products with the following substances: mercuric chloride,  $\text{C}_{21}\text{H}_{18}\text{Cl}_2 \cdot 2\text{HgCl}_2$ , metallic, green powder; phosphorus pentachloride,  $\text{C}_{21}\text{H}_{18}\text{Cl}_2 \cdot \text{PCl}_5$ ,  $\text{C}_6\text{H}_6$ , glistening, green, slender leaflets; phosphoryl chloride, glistening, green leaflets; stannic chloride, dark green powder with a green reflex; acetyl chloride, thionyl chlorid, and liquid sulphur dioxide, products forming green solutions. The ketochloride also forms green *salts* with sulphuric acid, nitric acid, and hydrogen chloride. The following derivatives of the ketochloride are prepared by methods similar to those already described: *chlorocarbinal*,  $\text{C}_{20}\text{H}_{18} \cdot \text{CCl} \cdot \text{OH}$ , long, white needles, m. p. 122°; *methyl ether*,  $\text{C}_{20}\text{H}_{18} \cdot \text{CCl} \cdot \text{OMe}$ , slender, white needles or glistening leaflets, m. p. 120.5°.

W. H. G.

Dibenzylideneacetone (Distyryl Ketone) and Triphenylmethane. VII. Nature of the Linking of the Halogen Atoms in the Ketohalides of Unsaturated Ketones. II. FRITZ STRAUS [and, in part, with JEAN B. KRIER and GEORG LUTZ] (*Annalen*, 1910, 374, 121—198. Compare this vol., i, 119 and preceding abstract; Straus and Ecker, *Abstr.*, 1906, i, 859; Straus and Caspari, 1907, i, 609; Straus and Ackermann, 1909, i, 489; Straus and Hüsey, *ibid.*, 490).—The ketohalides of *pp*-dimethoxybenzylideneacetophenons have been investigated. They resemble the halides already described, but are more reactive, owing to the presence of the methoxy-substituents. They also yield intensely coloured perbromides and periodides, analogous to those derived from the triphenylmethyl halides. Unlike most of the examples studied previously, it is found that the bromide has a lower m. p. than the chloride.

The chlorobromides have been prepared by the following methods:

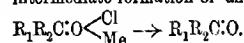


and the products obtained have been found to be identical. This has been proved by determining the amounts of halogen hydrides liberated

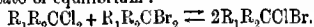
by the action of hydroxylic reagents, such as water and methyl alcohol, on the products. The amount of hydrogen bromide formed is much greater than the amount of hydrogen chloride (20%).

It is pointed out that the relative amounts of the two halogen hydracids vary with the constitution of the ketone from which the ketohalides are derived, and thus each case is characterised by a specific equilibrium of the two valency forms.

Water and methyl alcohol transform the ketodichlorides into the corresponding chlorocarbinal and its methyl ether, but these are spontaneously decomposed into the ketone, probably owing to the intermediate formation of an oxonium derivative:  $R_1R_2CCl \cdot OMe \rightarrow$



It is found that the keto-dichloride and -dibromide affect one another in solution. When freshly mixed, the solution yields molecular proportions of hydrochloric and hydrobromic acids, but the amount of hydrobromic acid increases at the expense of the hydrochloric, until an equilibrium is established, which is identical with that obtained when a solution of the ketochlorobromide has been kept for some time. The conclusion is drawn that the chlorobromide in solution decomposes to a slight extent into molecular quantities of dichloride and dibromide, and that the three halogen derivatives are present in solution in a state of equilibrium:



When evaporated the solution yields a product with all the properties of the chlorobromide, and this is its simplest method of formation; after purification, a solution of the product gives the usual relative amounts of hydrochloric and hydrobromic acids, but in the course of time returns to the above-mentioned equilibrium. Coloured intermediate products are not formed, and all the reactions are attributed to decompositions into colourless ions (compare Hantzsch and Meyer, this vol., i, 238):  $2CR_1R_2ClBr \rightleftharpoons CR_1R_2Cl^+ + CR_1R_2Br^- + Cl^- + Br^- \rightleftharpoons CR_1R_2Cl_2 + CR_1R_2Br_2$ .

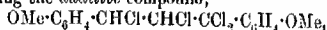
The solid chlorobromide is regarded as the pure compound,  $CR_1R_2ClBr$ , and dissociation is supposed to take place on fusion or solution.

The formation of the ketodibromide from the chlorobromide and bromine or hydrogen-bromide is not merely due to the relative amounts of the valency isomerides present, but also depends on the rapidity with which the equilibrium between the ketohalides is attained, and this varies with different ketones.

*Di-p-methoxyphenyl styryl ketone*,  $OMe \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot C_6H_4 \cdot OMe$  obtained by condensing acetylanisole (Abstr., 1890, 963) with anisaldehyde in the presence of sodium ethoxide (5% solution), crystallises in yellow prisms, m. p. 101–102°, and gives a reddish-yellow coloration with concentrated sulphuric acid. The compound with mercuric chloride,  $C_{17}H_{18}O_4 \cdot HgCl_2$ , forms golden-yellow needles, m. p. 150°, and is much more stable than the corresponding derivative of distyryl ketone. The *dibromide*,  $OMe \cdot C_6H_4 \cdot CHBr \cdot CHBr \cdot CO \cdot C_6H_4 \cdot OMe$ , forms snow-white crystals, m. p. 140° (decomp.), and when boiled with ten times its weight of methyl alcohol for twenty minutes yields the

methyl ether,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHBr}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , as colourless needles, m. p. 108—109°, which dissolve in concentrated sulphuric acid to cherry-red solutions.

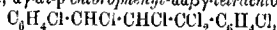
The *ketodichloride*, *p*-methoxyphenyl-*p*-methoxystyryldichloromethane,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , is best isolated as its additive compound with phosphorus pentachloride,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Cl}_2\cdot\text{PCl}_5$ , which forms steel-blue crystals. The ketodichloride crystallises from a mixture of carbon disulphide and light petroleum in brilliant colourless, compact prisms, melting at 78° to a green liquid. The compound,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Cl}_2\cdot 4\text{HgCl}_2$ , forms brownish-violet needles, and is most useful for characterising the chloride. The *hydrochloride*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Cl}_2\cdot\text{HCl}$ , forms slender, blue needles, and the *periodide*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Cl}_2\cdot\text{I}_2$ , dark crystals, m. p. 81—83°, which are partially decomposed by most solvents. The *sulphate* has not been obtained crystalline, and an additive compound with carbon disulphide has not been isolated. The ketochloride reacts with a carbon tetrachloride solution of chlorine, yielding the *additive* compound,



in the form of an unstable oil, which appears to be identical with the product obtained by the action of an excess of phosphorus pentachloride on a benzene solution of the ketone. A solution of bromine in carbon disulphide yields the *perbromide*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{ClBr}_2\cdot\text{Br}_2$ , in the form of a green precipitate, m. p. 120° (decomp.).

Thionyl chloride and phosphoryl chloride yield precipitates, but phosphorus trichloride, acetyl chloride, and nitriles do not. Nitriles yield pale blue solutions, and liquid sulphur dioxide an intense violet solution.

*p*-Chlorophenyl-*p*-chlorostyryldichloromethane (Abstr., 1909, i, 489) yields a *dichloride*,  $\alpha,\gamma$ -di-*p*-chlorophenyl- $\alpha,\beta$ -tetrachloropropane,



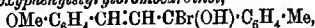
which crystallises from methyl alcohol in slender, colourless needles, m. p. 101°. The compound is formed slowly, and when reduced with active aluminium and sodium methoxide dissolved in methyl alcohol yields 4:4'-*dichlorophenylbenzylacetylene*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Cl}$ , as colourless plates, m. p. 80—80.5°.

*p*-Methoxyphenyl-*p*-methoxystyryldichloromethane reacts readily with water, and also with methyl alcohol, yielding 4:4'-*dimethoxyphenylstyryldichlorocarinol*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , and its methyl ether,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CCl}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ . The carbinol crystallises as colourless, felted needles, m. p. 75—76°, and the methyl ether as glistening, colourless plates, m. p. 44—45°. Both compounds are extremely unstable, and in their preparation it is necessary to avoid light and all traces of acid. The carbinol reacts readily with concentrated hydrochloric acid, regenerating the ketodichloride, and the methyl ether with glacial acetic acid yields the ketone.

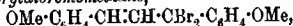
The *ketotribromide*, 4:4'-*dimethoxyphenylstyryldibromomethane*, cannot be prepared by the action of phosphorus pentabromide on the ketone or its hydrobromide, but can be obtained by the action of phosphorus tribromide on a benzene solution of the ketone. The reaction is slow, and is of use only with ketones containing a reactive carbonyl group, especially those containing methoxy-substituents. The ketobromide is

best isolated as its complex with mercuric bromide, or, in certain cases, as its additive compound with bromine, and can be obtained from the mercuric bromide compound by conversion into the bromocarbinal and treatment with hydrobromic acid.

4:4'-Dimethoxyphenylstyrylbromocarbinal,



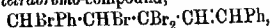
crystallises in long, colourless, felted needles, m. p.  $83-84^\circ$ , is only moderately stable, and is immediately decomposed by mineral acids, regenerating the ketone; with hydrobromic acid it yields 4:4'-dimethoxyphenylstyryldibromomethane,



which can be crystallised with some difficulty from a mixture of carbon disulphide and light petroleum. It forms long, lemon-yellow prisms, m. p.  $64^\circ$ , to a green liquid, and gives rises to the following derivatives:  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_2\cdot 3\text{HgBr}_2$ , small, violet needles; *perbromide*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_2\cdot\text{Br}_2$ , green crystals, m. p.  $128-130^\circ$ , can be obtained by the action of either bromine or phosphorus pentabromide on the ketodibromide; *periodide*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_2\cdot\text{I}_4$ , green crystals, m. p.  $104-106^\circ$  (decomp.); *hydrobromide*,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_2\cdot\text{HBr}$ , steel-blue needles, m. p.  $90-95^\circ$ ; *sulphate*, green, glistening needles; *nitrate*, steel-blue, sparingly soluble needles;  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}_2\cdot\text{SO}_2$ , bluish-green, glistening crystals. The ketodibromide also yields bluish-green, crystalline precipitates with solutions of zinc chloride, ferric chloride, and mercuric chloride in concentrated hydrochloric acid. Water or silver oxide and ether transform the ketodibromide into the bromocarbinal, glacial acetic acid transforms it into the ketone, and methyl alcohol transforms first into the methyl ether of the bromocarbinal (ons to two minutes) and ultimately (eight hours) into the ketone. The *methyl ether*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CBr}(\text{OMe})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , crystallises in colourless, glistening plates, m. p.  $39.5-40.5^\circ$ .

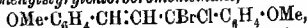
Phosphorus tribromide reacts with a boiling ethereal solution of di-*p*-methoxystyryl ketone, giving a quantitative yield of the *hydrobromide* of the ketone,  $\text{C}_{19}\text{H}_{18}\text{O}_3\cdot\text{HBr}$ , as a dark reddish-violet precipitate. Phosphorus tribromide, when boiled with a benzene solution of di-*p*-methoxystyryl ketone, yields di-*p*-methoxystyryldibromomethane, which can be isolated as its green complex with mercuric bromide. When this complex is shaken with a solution of potassium bromide in 66% methyl alcohol, di-*p*-methoxystyrylbromocarbinal methyl ether,  $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH})_2\text{CBr}\cdot\text{OMe}$ , is formed. It crystallises in snow-white plates, m. p.  $102-103^\circ$ , and its solution in concentrated sulphuric acid has a pure blue colour.

Phosphorus pentabromide reacts with a carbon disulphide solution of distyryl ketone or its hydrobromide, yielding the same products as does bromine itself (compare Vörlander and Siebsrt, Abstr., 1904, i, 900). With phosphorus tribromide, the ketodibromide is formed, and this can be isolated as the tetrabromo-compound,



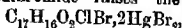
m. p.  $170^\circ$  (decomp.).

Di-*p*-methoxyphenylstyrylchlorobromomethane,



is more readily obtained by the action of hydrochloric acid on the

bromocarinol than by that of hydrobromic acid on the chlorocarinol, as the latter reaction is accompanied by side reactions. It crystallises in brilliant, lemon-yellow prisms, m. p.  $71^{\circ}$ , to a green liquid. Its addition to the ketodihromide raises the m. p. The complex,



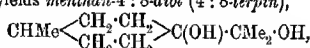
forms reddish-violet needles; the *perbromide*,  $C_{17}H_{16}O_2ClBr, Br_2$ , has m. p.  $122^{\circ}$  (decomp.); the *periodide* forms a brilliant green, crystalline precipitate, m. p.  $102-104^{\circ}$  (decomp), and the *hydrobromide*, steel-blue needles, and in its preparation a portion of the chlorine becomes replaced by bromine. The additive compound with sulphur dioxide forms green, metallic, glistening crystals, which are unstable. The ketodihromide and the chlorohromide are not affected when shaken with dry benzene and silver chloride.

J. J. S.

Terpenes and Ethereal Oils. CII. OTTO WALLACH (*Annalen*, 1910, 374, 217—235).—I. *Preparation of Hydroxy-ketones and 1:2-Glycols from the Nitroschlorides of Semicyclic Hydrocarbons.*—

Both of the nitroschlorides derived from 1-methyl-4-ethylidencyclohexane react with a mixture of anhydrous sodium acetate and glacial acetic acid at  $63-70^{\circ}$ , yielding the oxime of 4-acetoxy-1-methylcyclohexyl methyl ketone,  $CHMe \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{OAc}) \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$ , m. p.  $111-112^{\circ}$ , together with the oxime of *p*-acetyl-methylcyclohexene; the latter compound is also formed when the oxime melting at  $111-112^{\circ}$  is distilled.

When the oxime is hydrolysed with 5% sulphuric acid, 4-hydroxy-4-acetylhexahydrotoluene (4-hydroxy-1-methylcyclohexyl methyl ketone),  $CHMe \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C}(\text{Ac}) \cdot \text{OH}$ , is formed. It has h. p.  $223-224^{\circ}$  and m. p.  $21-22^{\circ}$ , and is only sparingly volatile in steam; its *semicarbazone* crystallises in plates, m. p.  $219-220^{\circ}$ , and its *oxime* has m. p.  $128^{\circ}$ . When boiled with 20% sulphuric acid, the hydroxy-ketone yields *p*-acetyl-methylcyclohexene, and when treated with magnesium methyl iodide yields *menthan-4:8-diol* (4:8-terpin),



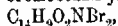
which exists in two stereoisomeric forms, melting respectively at  $97-98^{\circ}$  and  $82-83^{\circ}$ . The less fusible compound has h. p.  $245^{\circ}$ , and yields a liquid bromide; when oxidised, it yields *p*-methylcyclohexanone. The glycol, m. p.  $82-83^{\circ}$ , is more readily soluble than its isomeride, and both compounds are readily volatile in steam.

11. *The Terpinene Question* (compare Wallach, *Abstr.*, 1907, i, 1058; 1908, i, 813; Auwers and Heyden, *Abstr.*, 1909, i, 593; Müller, Walbaum, and Müller, *Schimmel's Ber.*, 1909, ii, 16, 33).—A brief summary of researches on terpinenes. It is pointed out that all terpinenes, even that obtained from terpinene dihydrochloride, contain both  $\Delta^{1:3}$ -dihydro-*p*-cymene and the isomeric  $\Delta^{1:4}$ -compound. The presence of the former has been established by its conversion into  $\Delta^2$ -dihydroxy- $\alpha$ -methyl- $\beta$ -isopropyladipic acid, and it is this constituent of the terpinene which yields the nitrosite, m. p.  $155^{\circ}$ . The presence of  $\Delta^{1:4}$ -dihydro-*p*-cymene has been proved by its oxidation to the

erythritol (1 : 2 : 3 : 4-tetrahydroxyterpane), which can be transformed by loss of water into a mixture of carvacrol and thymol (Gildmeister and Müller, *Schimmel's Ber.*, 1909, ii, 16).  $\alpha$ -Terpinene =  $\Delta^{1:3}$ -dihydro-*p*-cymene =  $\Delta^{1:2}$ -menthadiene = carvenene (Semmler).  $\beta$ -Terpinene =  $\Delta^{1:4}$ -menthadiene;  $\gamma$ -terpinene =  $\Delta^{1:4}$ -dihydro-*p*-cymene =  $\Delta^{1:4}$ -menthadiene = isocarvenene (Semmler). So far, neither  $\Delta^{1:3}$  nor  $\Delta^{1:4}$  menthadiene has been obtained free from its isomeride, and the same appears to hold good for all doubly-unsaturated cyclic hydrocarbons.

J. J. S.

*pp*-Dibromobenzil. HEINRICH BILTZ, H. EDLEFSEN, and KARL SEYDEL (*Ber.*, 1910, 43, 1815—1820. Compare Biltz, *Abstr.*, 1908, i, 575; 1909, i, 839).—Di-*p*-bromobenzil yields a monoxime,



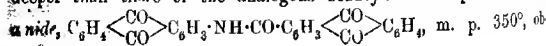
in the form of minute, colourless needles, m. p. 159—160°, and a phenylhydrazone,  $C_{17}H_{11}ON_2Br$ , m. p. 189°. It does not yield a semicarbazone, but forms 3-oxo-5:6-di-*p*-bromophenyl-2:1:4-triazine,  $C_8H_4Br_2C:N:C:N$ , when heated with semicarbazide hydrochloride and dilute acetic acid. This crystallises in colourless needles, m. p. 253°, and yields a sodium derivative,  $C_{15}H_8ON_2Br_2Na$ , in the form of pale yellow prisms, and an acetyl derivative,  $C_{17}H_{11}O_2N_2Br_2$ , in the form of hexagonal, colourless plates, m. p. 283°, which are readily hydrolysed.

Di-*p*-bromobenzilic acid,  $OH\cdot C(C_6H_4Br)_2\cdot CO_2H$ , prepared by the action of an alcoholic solution of sodium ethoxide on the dibromobenzil at the ordinary temperature, crystallises from a mixture of chloroform and light petroleum in needles, m. p. 108—110°, and when heated with carbamide at 220° yields 5:5-dibromophenylhydantoin. When heated for three to four hours at 180°, the acid loses carbon dioxide and yields di-*p*-bromobenzhydrol,  $OH\cdot CH(C_6H_4Br)_2$ , which crystallises in glistening, colourless plates, m. p. 174—175°.

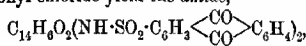
Di-*p*-bromotriphenylacetic acid,  $CH(C_6H_4Br)_3\cdot CO_2H$ , obtained by reducing the benzilic acid with hydriodic acid and red phosphorus in the presence of acetic acid, crystallises in needles, m. p. 187—188°.

Dibromodeoxybenzoin,  $C_6H_4Br\cdot CO\cdot CH_2\cdot C_6H_4Br$ , obtained by reducing dibromobenzil with zinc dust and glacial acetic acid, crystallises in long, brittle needles, m. p. 141—142°, and does not yield an oxime, a phenylhydrazone, or a semicarbazone. J. J. S.

**Acylated Aminoanthraquinones and Anthraquinone Mercaptans and their Behaviour on Vegetable Fibres.** CHR. SEGA and R. WEITZENBÖCK (*Monatsh.*, 1910, 31, 371—377).—Recently vat-dyes of the anthraquinone series have been obtained by the action of benzoyl chloride on aminoanthraquinones dissolved in nitrobenzene (*Chem. Zeit.*, 1909, No. 108). The authors have now prepared acylated aminoanthraquinones in a similar manner, and find that they are pronounced vat-dyes, giving on unmordanted cotton tones which are deeper than those of the analogous benzoylated compounds. The

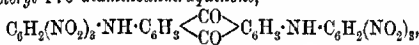


tained by heating 2-aminoanthraquinone and the chloride of anthraquinone-2-carboxylic acid in nitrobenzene for half an hour, forms pale yellow crystals, and in the hyposulphite vat produces feeble yellow tones on unmordanted cotton. The *amides*, obtained from the same acid chloride and 1:5-, 1:3-, and 1:8-diaminoanthraquinones respectively, produce on unmordanted cotton in the hyposulphite vat brown to brownish shades, which are changed to brown to brick-red by atmospheric oxidation. The *amide*,  $C_{23}H_{15}O_6NS$ , m. p.  $257^\circ$ , obtained from 1-aminoanthraquinone and anthraquinone-2-sulphonyl chloride, yields a dark red vat, which produces brown shades changing to faint greyish-green by oxidation. 1:5-Diaminoanthraquinone and anthraquinone-2-sulphonyl chloride yield the *amide*,



m. p.  $391^\circ$ , the vat of which is dark red, producing faint red shades changing to light yellow by oxidation.

1:5-Diaminoanthraquinone and picryl chloride in nitrobenzene yield *dipicryl-1:5-diaminoanthraquinone*,

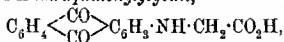


which decomposes above  $340^\circ$ , and forms a brown vat in alkaline hyposulphite, which produces dark green shades on unmordanted cotton; these shades are changed by oxidation to violet, which are turned brown by the addition of dilute hydrochloric acid.

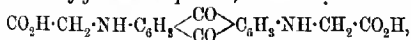
Anthraquinone-1-thiol and benzoyl chloride in nitrobenzene yield *benzoylanthraquinone-1-thiol*,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} C_6H_3 \cdot SBz$ , m. p.  $208^\circ$ , which forms yellow crystals, and has not the slightest affinity for vegetable fibres.

**Action of Benzyl Chloride and of Monochloroacetic Acid on Aminoanthraquinones.** CHE. SEER and R. WEITZENBÜCK (*Monatsh.*, 1910, 31, 379—386).—In view of the fact that the introduction of acyl groups into the amino-groups of aminoanthraquinones converts these coloured but non-dyeing substances into strong dyes, the effect of the introduction of benzyl, *p*-chlorobenzyl, and glycino-groups has been examined. The products do not possess the character of vat-dyes.

1-Benzylaminoanthraquinone, m. p.  $189^\circ$ , obtained from 1-aminoanthraquinone and benzyl chloride at  $170$ — $175^\circ$ , forms red needles, and is reduced by alkaline hyposulphite to the corresponding dihydroanthraquinone. 1-Anthraquinonylglycine,



m. p.  $218$ — $226^\circ$  (decomp.), obtained from 1-aminoanthraquinone, anhydrous sodium acetate, and chloroacetic acid at  $170^\circ$ , is a brick-red powder. 1:5-Diglycinoanthraquinone,



obtained from 1:5-diaminoanthraquinone in a similar manner, is a dark red powder, which dyes wool directly, and dissolves in alkalis with an extremely deep reddish-violet colour.



1:5-Dibenzylaminoanthraquinone, m. p. 225°, and 1:5-di-p-chlorobenzylaminoanthraquinone, m. p. 271—272°, are remarkable in that they are not converted into the corresponding dihydroanthraquinones by alkaline reducing agents. Dibenzoyl-1:5-dibenzylaminoanthraquinone,  $C_{28}H_{20}O_4N_2$ , m. p. 293°, prepared from 1:5-dibenzylaminoanthraquinone and benzoyl chloride at 90—100°, crystallises in red leaflets.

C. S.

**Relation between Molecular Constitution and Odour.** GÉZA AUSTERWEIL and G. COCHIN (*Compt. rend.*, 1910, 150, 1693—1695).—Citronellol, 1-methylcitronellol, and 1:1-dimethylcitronellol have distinct rose-like odours. The latter compound was obtained by oxidising 1-methylcitronellol and treating the resulting ketone by Grignard's method; it has b. p. 113—116°/24 mm.,  $[\alpha]_D - 11^{\circ}38'$ . 1-Ethylcitronellol, b. p. 125—130°/22 mm.,  $[\alpha]_D - 11^{\circ}26'$ , and 1:1-diethylcitronellol, h. p. 119—123°/20 mm.,  $[\alpha]_D - 13^{\circ}25'$ , have well-marked, rose-like odours. The odour is less distinct in 1-propylcitronellol, b. p. 118—122°/22 mm., and 1-butylcitronellol, b. p. 105—108°/16 mm. Introduction of a phenyl group intensifies the odour; 1-phenylcitronellol has b. p. 102—104°/12 mm.

An odour of roses appears to be associated with the presence of the group  $-CH_2 \cdot CRR' \cdot OH$ ; the presence of an ethylenic linking also appears to be essential.

W. O. W.

**A New Tertiary Menthol; Conversion of Pinene into Menthene.** AUGUSTE DÉHAL (*Compt. rend.*, 1910, 150, 1762—1765).—Haller and Martine (*Abstr.*, 1905, i, 533) obtained hexahydrocymene by the reduction of terpineol; employing the same method, but under different conditions, the present author has converted terpineol into a tertiary menthol,  $CHMe \cdot \begin{smallmatrix} CH_3 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} > CH \cdot CMe_2 \cdot OH$ .

The product is optically inactive, and does not appear to be a mixture of *cis*- and *trans*-isomerides; it has b. p. 99—100°/17 mm., 206—208° under atmospheric pressure;  $D_{20}^{20} 0.912$ ;  $n_D^{20} 1.46874$ . The phenylurethane has m. p. 94—95°; the acetate has h. p. 104°/16 mm. Acetic acid in presence of sulphuric acid transforms the menthol into  $\Delta^{40}$  menthene (Wallach, *Abstr.*, 1905, i, 407; Auwers, this vol., i, 122). Oxidation with mercuric oxide and iodine, followed by treatment with silver nitrate, converts this hydrocarbon into menthones.

W. O. W.

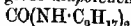
**Constitution of Fenchone.** LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 542—548).—A résumé of work already published (*Abstr.*, 1908, i, 193). The fenchone used was isolated by fractional distillation from the crude fenchone obtained from fennel oil. On treatment with sodamide until no further action took place, a residue containing camphor was obtained.

T. A. H.

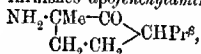
**Constitution of Fenchone. II.** LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 683—687).—A résumé of

work already published in part (Abstr., 1908, i, 193; 1909, i, 497, 595). The following new data are given. Dihydrofencholenic acid, b. p. 162–165°/23 mm., obtained by hydrolysis of the amide with 30% potassium hydroxide in alcohol, does not solidify when pure (compare Semmler, Abstr., 1906, i, 681). The *chloride* has b. p. 105°/20 mm. The *anhydride*, h. p. 205–210°/20 mm., D<sup>4</sup> 0.9841, obtained by warming the acid with acetic anhydride, is a colourless, thick liquid.

Dihydrofencholenamide, C<sub>9</sub>H<sub>17</sub>·CO·NH<sub>2</sub>, on treatment with bromine and potassium hydroxide, gives dihydrofenchylcarbamide,



(Abstr., 1908, i, 193), but if the alkali is replaced by sodium methoxide, the corresponding *methylurethane*, C<sub>11</sub>H<sub>21</sub>O<sub>2</sub>N, b. p. 142°/23 mm., colourless liquid of pleasant odour, is obtained. This is very stable to alkalis, but on prolonged heating with 30% potassium hydroxide in alcohol at 150° it furnishes *apofenchylamine*,



h. p. 68°/18 mm. or 173°/760 mm., which has a strong odour and rapidly absorbs carbon dioxide, forming a snow-white mass. The corresponding *carbamide*, C<sub>9</sub>H<sub>17</sub>·NH·CO·NH<sub>2</sub>, m. p. 129–130°, crystallises in slender needles from acetic acid.

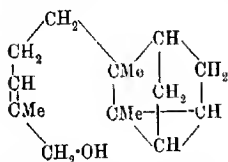
T. A. H.

**Constituents of Ethereal Oils. Further Degradation of Eriksantalnic Acid.** FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 910, 43, 1890–1892. Compare this vol., i, 495, and following abstract).—Methyl noreksantalate is converted by sodium and alcohol into *noreksantalol*, C<sub>11</sub>H<sub>18</sub>O, b. p. 114–117°/10 mm., D<sup>20</sup> 0.9958,  $n_D^{20}$  1.49049,  $\alpha_D^{20}$  –0.7° (100 mm. tube), a benzene solution of which is oxidised by potassium dichromate and dilute sulphuric acid to *noreksantalal*, C<sub>11</sub>H<sub>16</sub>O, h. p. 92–94°/11 mm., D<sup>20</sup> 0.9964,  $n_D^{20}$  1.48301,  $n_D^{20}$  –30.8° (100 mm. tube), the *semicarbazone* of which has m. p. 224°. The CHO group of the aldehyde must be attached to a methylene group, because *enol-noreksantalal acetate*, C<sub>11</sub>H<sub>15</sub>·OAc, b. p. 110–113°/0 mm., D<sup>20</sup> 1.0270,  $n_D^{20}$  1.48374,  $\alpha_D^{20}$  –25.6° (100 mm. tube), obtained from the aldehyde, acetic anhydride, and sodium acetate, is oxidised in acetone solution by potassium permanganate to *tereksantalnic acid*, C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>. The formation of this acid, which contains 10 atoms of carbon, is another proof that the compounds of the noreksantalnic acid series contain 11 atoms of carbon; numbers of the eksantalnic acid series contain 12 atoms of carbon. In all three series occurs the same tricyclic system as is present in  $\alpha$ -santalol.

C. S.

**Constituents of Ethereal Oils. Constitutions of the Santalol and of the  $\alpha$ -Santalene Series, and of Sesquiterpene Alcohols and of Sesquiterpenes.** FRIEDRICH W. SEMMLER (*Ber.*, 910, 43, 1893–1898).—"Santalol," obtained by distilling oil of sandal-wood with steam, converting the oil in the distillate into the hydrogen phthalate, and hydrolysing the ester, is a mixture of two

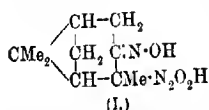
primary alcohols:  $C_{15}H_{24}O$ , which can be tolerably satisfactorily separated by repeated fractionation into  $\alpha$ -santalol, b. p. 159—160°/10 mm.,  $D^{20}_D$  0.978,  $n_D$  1.498,  $\alpha_D$  1° (100 mm. tube), and  $\beta$ -santalol, b. p. 167—168°/10 mm.,  $D^{20}_D$  0.9715,  $n_D$  1.509,  $\alpha_D$  -42° (100 mm. tube). The molecular refraction of the "santalol," regenerated from the hydrogen phthalates, indicates the presence therein of a singly unsaturated tricyclic alcohol and a doubly unsaturated dicyclic alcohol. The assumption that the former is  $\alpha$ -santalol and the latter  $\beta$ -santalol is justified by the results of oxidising "santalol."



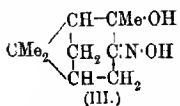
potassium permanganate gives tricyclic eksantallic acid,  $C_{12}H_{18}O_2$ , and oxidation by ozone gives tricyclic eksantalal,  $C_{12}H_{18}O$ ; the yields of the acid and of the aldehyde are best in the lower-boiling fractions, that is, those rich in  $\alpha$ -santalol. Eksantalal has been converted into teresantallic acid (preceding abstract), the constitution of which is known. The author gives reasons for assigning to teresantallic acid a constitution based on the camphor type, not on the camphene type. Consequently, eksantalal, eksantallic acid, and therefore the sesquiterpene alcohol,  $\alpha$ -santalol, have constitutions based on the camphor type. The last-mentioned alcohol has the annexed constitution.

C. S.

#### $\alpha$ -Pineneisonitroamineoxime and Its Decomposition Products. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 747—753. Compare this vol., i, 182).—

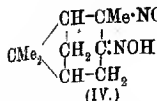


Nitrous acid reacts with the hydroxylamine-group of  $\alpha$ -pinenehydroxylamineoxime, forming the isonitroamineoxime, I, which is fairly stable when dry. When suspended in water and heated on the water-bath, however, it is converted into hydroxydihydrocarvoxime, II (compare Wallach, *Abstr.*, 1896, i, 571), and nitrous oxide. A similar decomposition is effected by dilute acetic acid. Alkalis act differently, however, for they yield nitrous acid, nitrosopinene, and hydroxypinocampheoxime, III (the oxime of pinene hydrate). A substance, m. p. 70—80°, is also formed, but it is not crystalline. Since pineneisonitroamineoxime yields hyponitrous acid (or nitrous oxide and water), however, it may be decomposed; it appears that the substance reacts as though it had the formula IV (compare this vol., i, 182).

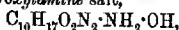


$\alpha$ -Pineneisonitroamineoxime is obtained by the action of an aqueous solution of sodium nitrite on an aqueous solution of the hydrochloride or sulphate of pinene-*o*-hydroxylamineoxime; it forms large, colourless prisms, m. p. 127° (decomp.), dissolves in alkali carbonates, gives Liebermann's reaction, and a wine-red coloration

with ferric chloride. The sodium salt, prepared with the aid of sodium ethoxide, decomposes at 92—95°.



The hydroxylamine salt,



crystallises in lustrous prisms, m. p. 110° (decomp.); it reduces Fehling's solution in the cold, and barely shows Lieber-

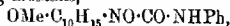
mann's reaction. *o*-Hydroxypinocampheoxime, which is best obtained (yield 20%) by the slow decomposition of the sodium salt of the isonitroamine at the ordinary temperature, crystallises in lustrous, rhombic prisms, m. p. 128° (softening a few degrees previously). The substance resists prolonged boiling with aqueous or alcoholic solutions of alkaline hydroxides, but it is at once attacked by acids. When treated with hydrochloric acid, even in the cold, it loses its oximic group. Dilute acetic acid does not affect the oximic group, but converts the compound completely into hydroxydihydrocarvixime.

R. V. S.

**Sesquiterpenes. IV. ERNST DEUSSEN** [with HANS PHILIPP] (*Annalen*, 1910, 374, 105—120. Compare *Abstr.*, 1909, i, 813).—**A. Gurjun balsam oil.**—This oil varies considerably in composition, and contains at least two distinct sesquiterpenes, named provisionally,  $\alpha$ - and  $\beta$ -gurjunene.  *$\alpha$ -Gurjunene* is a strongly laevorotatory oil, b. p. about 119°/1 mm., and is probably a bicyclic sesquiterpene.  *$\beta$ -Gurjunene* is a slightly dextrorotatory oil, b. p. about 122.5—123.5°/12 mm., and is probably a tricyclic compound. Both sesquiterpenes, when oxidised by potassium permanganate, yield a ketone,  $\text{C}_{15}\text{H}_{24}\text{O}$ , a colourless oil, b. p. 175—178°/12 mm.,  $n_D^{20} + 120$ —130°,  $D_4^{20} 1.0160$ ,  $n_D^{20} 1.5303$ ; the oxime of the ketone is pale yellow, and has b. p. 204°/12 mm. Gurjun balsam oil, when treated with hydrogen chloride and subsequently with anhydrous sodium acetate and glacial acetic acid, yields *isogurjunene*, a bicyclic sesquiterpene, b. p. 129.5—132°/12 mm., which when oxidised does not yield a ketone forming a crystalline semicarbazone.

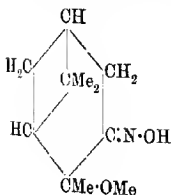
**B. "Caryophyllene."**—The substance m. p. 125—125.5°, which was isolated from the mother liquor obtained in the preparation of  *$\alpha$ -caryophyllene nitrosochloride* (*loc. cit.*), is shown to be a *nitrosoethoxycaryophyllene*,  $\text{OEt}\cdot\text{C}_{15}\text{H}_{24}\cdot\text{NO}$ .

**Monoterpenes.—I.** The substance obtained by the action of sodium methoxide on pinene nitrosochloride (*loc. cit.*) is *oximinomethoxyhydro-pinene* (annexed formula). It is converted (1) by phenyl carbimide into the corresponding *urethane*,

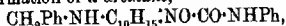


which crystallises in rosettes of needles, m. p. 102°, and (2) by an alcoholic solution of hydrogen chloride into *i*-chlorohydrocarvixime.

Nitrosopinene, when treated with phenyl carbimide, yields the corresponding *urethane*,  $\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2$ , m. p. 101—102°.



II. Pinene nitrosochloride as usually prepared, when washed with ethyl alcohol, yields a dextrorotatory solution in chloroform, and when treated with benzylamine yields a nitrolhenzylamine, together with a substance (pinenenitrolhenzylamine?) which crystallises in needles, m. p. 148—149°,  $[\alpha]_D + 96.7^\circ$  (1.191% solution in ethyl acetate). The presence of an oximino-group in pinenenitrolbenzylamine is demonstrated by the formation of a urethane,



m. p. 189.5—190° (decomp.), when it is treated with phenylcarbimide.

W. H. G.

Scutellarin. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Monatsh.*, 1910, 31, 439—491. Compare Goldschmiedt and Molisch, *Abstr.*, 1902, i, 48).—An amplification of work already recorded. The formula  $\text{C}_{21}\text{H}_{20}\text{O}_{12}$ , previously attributed to scutellarin, is altered to  $\text{C}_{21}\text{H}_{18}\text{O}_{12}$ , as a consequence of further analysis and of its hydrolysis to scutellarein and glycuronic acid. Scutellarin is shown to be homogeneous by extraction with methyl alcohol, whereby only a slight black powder, chiefly inorganic, remains; the substance in the alcoholic solution is fractionally crystallised, yielding fractions having practically the same properties. The colour reaction with  $\alpha$ -naphthol and sulphuric acid is shown to be characteristic of glycuronic acid. By titration with  $N/10$ -potassium hydroxide and phenolphthalein, by estimating the carbon dioxide liberated from barium carbonate by scutellarin, and by the analysis of the barium salt, scutellarin is proved to contain one carboxyl and one phenolic hydroxyl group. The acetate, m. p. 263—265° (decomp.), contains five acetyl groups, and regenerates scutellarin by hydrolysis. When oxygen is passed for four days into a solution of scutellarin in 25% potassium hydroxide, the ethereal extract of the resulting solution contains *p*-hydroxyacetophenone.

The hydrolysis of scutellarin is best effected by adding concentrated sulphuric acid to a rapidly stirred suspension of finely powdered scutellarin in water until solution is complete, and then pouring the mixture into cold water. The operation requires only thirty to forty seconds, a quantitative precipitate of scutellarein is obtained, and the filtrate contains glycuronic acid.

Scutellarein,  $\text{C}_{15}\text{H}_{10}\text{O}_6$ , is undoubtedly a flavone derivative by reason of its behaviour as a mordant dye, its property of forming salts with metals or acids, and the nature of its products of decomposition by alkalis. It is oxidised by boiling 14—15% nitric acid to picric, oxalic, and 3:5-dinitro-4-hydroxybenzoic acids. By acetylation it yields a tetra-acetate,  $\text{C}_{15}\text{H}_6\text{O}_6(\text{OAc})_4$ , m. p. 235—237°.

Methylation by ethereal diazomethane yields scutellarein trimethyl ether,  $\text{C}_{15}\text{H}_7\text{O}_3(\text{OMe})_3$ , m. p. 189—190°, whilst the action of methyl iodide and methyl-alcoholic potassium hydroxide results in the formation of the trimethyl ether, together with a small amount of a tetramethyl ether, m. p. 158—160°.

The hydrolysis of scutellarein by boiling 12% potassium hydroxide or by fusion with potassium hydroxide yields *p*-hydroxyacetophenone, *p*-hydroxybenzoic acid, and a substance which gives the pine-shaving reaction of phloroglucinol.

The preceding results are explained by regarding scutellarein as 1:3:4:4'-(or 1:2:3:4')-tetrahydroxyflavone, and scutellarin provisionally as  $R \cdot O \cdot CH \cdot [CH \cdot OH]_2 \cdot CH \cdot CH(OH) \cdot CO_2H$ , where R



represents the scutellarein residue.

C. S.

Cornin, the Bitter Principle of Cornus Florida. EMERSON R. MILLER (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, 7, xlii—xliii).—The best yields are obtained from the root-bark. It crystallises in colourless, silky needles or rectangular plates, m. p. 181°, and has neither basic nor acidic properties. Its aqueous solutions do not yield precipitates with silver nitrate or lead subacetate, but when kept for some time they reduce Fehling's solution, and when heated with a little alkali reduce Fehling's solution immediately. The aqueous solution also gives Pettenkofer's test for dextrose. It appears to be a glucoside with the composition represented by the formula  $C_{17}H_{24}O_{10}$  or  $C_{16}H_{21}O_9 \cdot OMe$ .

J. J. S.

Action of Phosphorus Pentachloride on Picrotin. PAUL HORMMANN (*Ber.*, 1910, 43, 1903—1907).—Phosphorus pentachloride acts as a dehydrating agent on picrotin in boiling chloroform, converting it into anhydropicrotin,  $C_{15}H_{16}O_8$ , m. p. 317° (decomp.), which does not reduce Fehling's solution or ammoniacal silver oxide solution, forms a benzoate,  $C_{22}H_{20}O_7$ , m. p. 250°, an acetate,  $C_{17}H_{18}O_7$ , m. p. 237°, and a diacetate,  $C_{19}H_{20}O_8$ , m. p. 192.5°, and dissolves in hot *N*/10-sodium hydroxide, the solution after acidification yielding anhydropicrotinic acid,  $C_{15}H_{18}O_7 \cdot H_2O$ , which decomposes at 221°, or in the anhydrous state at 233°.

The chloroform mother liquor contains a halogenated substance, which by prolonged boiling with methyl alcohol is converted into a substance,  $C_{15}H_{21}O_3P$ , m. p. 211°, which has not been further examined.

C. S.

Picrotoxin. FRANCESCO ANGELICO (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 473—480. Compare this vol., i, 404). The reduction of  $\alpha$ -picrotinic acid with hydriodic acid and red phosphorus yields, not only the acid,  $C_{15}H_{18}O_4$ , previously described (*loc. cit.*), but also a ketone, which from the composition of its oxime should have the formula  $C_{14}H_{10}O_3$ . When picrotoxin is heated with hydrochloric acid (of D 1.12, diluted with an equal volume of water) in a sealed tube for five hours at 170—180°, it also gives a ketone,  $C_{14}H_{15}ClO_3$ , which results from the substitution of an hydroxyl group by chlorine and loss of carbon dioxide. Picrotin yields the same substance, losing at the same time the molecule of water by which its formula differs from that of picrotoxin, so that both substances must contain the same nucleus. The ketone crystallises in small needles, m. p. 114—115°; it is insoluble in alkalis, and it forms an osazone, m. p. 196°, which does not contain halogen.

In order to obtain an indication of the presence of an aromatic nucleus, which from other reasons is probable, picrotinic acid,  $C_{15}H_{18}O_4$ , was nitrated with a mixture of equal volumes of concentrated

sulphuric acid and nitric acid (D 1.48). A nitro-derivative,  $C_{13}H_{15}O_5N$ , was obtained; it crystallises in pale yellow needles, m. p.  $166^\circ$ , and is very stable towards oxidising agents. A small quantity of a substance insoluble in alkali was also formed; it had m. p. about  $110^\circ$ . When the above nitro-derivative was reduced with ammonium sulphide, another nitro-compound was formed, m. p.  $173^\circ$  (previously softening).  
R. V. S.

**Method of Preparing Dimethylpyrone.** ZDENKO H. SRNAUF and J. PRIGLINGER (*Monatsh.*, 1910, 31, 363—369).—A mixture of 95 grams of acetic anhydride and 20 c.c. of sulphuric acid is boiled for four hours, and distilled as completely as possible in a vacuum. The solution of the residue in saturated ammonium sulphate is faintly basified by ammonium hydroxide, filtered, and repeatedly extracted with benzene. The extracts contain about 4 grams of 2:6-dimethylpyrone, m. p.  $132$ — $133^\circ$ . It is shown that the pyrone does not exist as such in the acetic anhydride.

In still poorer yield dimethylpyrone is obtained by heating acetic anhydride with phosphoric oxide, or by heating a mixture of acetyl chloride, glacial acetic acid, and sulphuric acid.

Dimethylpyrone is easily converted into luidone by dissolving it in a little water, saturating the solution with ammonia, and heating the mixture in a sealed tube for eight hours in a water-bath. C. S.

**Synthesis of 2:3-Dihydroxyflavone.** J. REIGRODSKI and JOSEF TAMBOR (*Ber.*, 1910, 43, 1961—1968).—Hydroxyquinol trimethyl ether reacts with acetyl chloride in the presence of aluminium chloride and carbon disulphide, yielding 2:4:5-trimethoxyacetophenone,  $C_6H_2(OMe)_3 \cdot COMe$ , which crystallises from alcohol in small, colourless needles, m. p.  $102$ — $103^\circ$ . The ketone reacts with methyl benzoate and sodium (granulated) at  $115$ — $120^\circ$ , yielding 2:4:5-trimethoxybenzoylacetophenone,  $COPh \cdot CH_2 \cdot CO \cdot C_6H_2(OMe)_3$ , which crystallises in small, ochre-yellow prisms, m. p.  $105^\circ$ . It gives a dark green coloration with ferric chloride, and when boiled for four hours with concentrated hydriodic acid yields 2:3-dihydroxyflavone,  $C_{15}H_{11}(OH)_2 \cdot \begin{smallmatrix} O-CPh \\ | \\ CO-CH \end{smallmatrix}$ ,

which crystallises from dilute alcohol in colourless, microscopic prisms, containing  $1H_2O$ , and with m. p.  $135^\circ$  (decomp.). Its diacetyl derivative,  $C_{19}H_{15}O_6$ , crystallises in thin needles, m. p.  $195^\circ$ , and its dimethyl ether,  $C_{17}H_{14}O_4$ , in slender, colourless needles, m. p.  $189^\circ$ .

2:4:5-Trimethoxyacetophenone condenses with aldehydes, yielding chalcone derivatives (Abstr., 1904, i, 426). With benzaldehyde it yields 2:4:5-trimethoxychalcone,  $C_{16}H_{12}(OMe)_3 \cdot CO \cdot CH : CHPh$ , which crystallises in canary-yellow needles, m. p.  $113$ — $114^\circ$ . Its solution in concentrated sulphuric acid is orange-coloured, and its dibromide,  $C_{18}H_{18}O_4Br_2$ , crystallises in pale yellow, prismatic plates, m. p.  $148^\circ$  (decomp.).

2-Hydroxy-2':4':5'-trimethoxybenzylideneacetophenone (2-hydroxy-2':4':5'-trimethoxychalcone),  $OH \cdot C_6H_3 \cdot CH : CH \cdot CO \cdot C_6H_2(OMe)_3$ , obtained by condensing salicylaldehyde with trimethoxyacetophenone

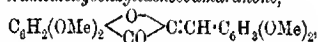
and alkali, crystallises<sup>†</sup> in green needles, m. p. 159—160° (decomp.). The *acetyl* derivative,  $C_{20}H_{18}O_6$ , crystallises in glistening, golden needles, and the *acetyl-dibromide*,  $C_{20}H_{16}O_6Br_2$ , forms colourless needles, m. p. 132° (decomp.). The latter compound reacts with alcohol and concentrated potassium hydroxide solution, yielding. 2':4':5'-

trimethoxy-1-benzoylcoumarone,  $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CH \end{smallmatrix} > C \cdot CO \cdot C_6H_3(OMe)_3$ , which crystallises from dilute alcohol in prismatic, yellow needles, m. p. 125°. Its solution in concentrated sulphuric acid is orange-coloured.

J. J. S.

1:3-Dimethoxycoumaranone. H. DUMONT and JOSEF TAMBOR (*Ber.*, 1910, 43, 1969—1971).— $\alpha$ -Bromophloracetophenone trimethyl ether (1:3:5-trimethoxy-1-bromoacetylbenzene),  $C_6H_2(OMe)_3 \cdot CO \cdot CH_2Br$ , obtained by the Friedel-Crafts synthesis from bromoacetyl bromide and phloroglucinol trimethyl ether, crystallises in colourless needles, m. p. 126°, and when boiled with alcoholic potassium acetate (compare Blom and Tambor, *Abstr.*, 1905, i, 916) yields 1:3-dimethoxycoumaranone,  $C_6H_2(OMe)_2 \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} > CH_2$ , which is identical with Friedländer and Schnell's dimethoxyketocoumaran (*Abstr.*, 1898, i, 24).

1:3:2':3'-Tetramethoxybenzylidenecoumaranone,

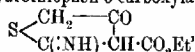


obtained by condensing 1:3-dimethoxycoumaranone with *o*-veratraldehyde and alkali, crystallises in yellow needles, m. p. 166°. Its solution in concentrated sulphuric acid is dark orange-coloured.

The isomeric 1:3:2':4'-tetramethoxy-compound, obtained from 1:3-dimethoxycoumaranone and 2:4-dimethoxybenzaldehyde, forms yellow needles, m. p. 209°; its solution in concentrated sulphuric acid is blood red. The 1:3:3':4'-tetramethoxy-derivative has m. p. 175°, and also yields a blood-red solution in sulphuric acid.

J. J. S.

Sulphur Derivatives of Ethyl Chlorocyanoacetate. ERICH BENARY (*Ber.*, 1910, 43, 1943—1956. Compare *Abstr.*, 1908, i, 600).—Ethyl  $\gamma$ -chloro- $\alpha$ -cyanoacetate reacts with an aqueous 15% solution of potassium hydrogen sulphide, yielding crystals of ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate,

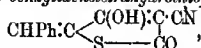


and ethyl thioisocyanoacetate,  $S[CH_2 \cdot CO \cdot CH(CN) \cdot CO_2Et]_2$ , which remains dissolved in the alkaline solution, and is precipitated on the addition of dilute sulphuric acid.

Ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate crystallises in flat, silvery needles, m. p. 219—220° (decomp.), after turning brown at 200°. It dissolves in dilute sodium hydroxide solution, but is rapidly decomposed. The *diacetyl* derivative,  $C_{11}H_{13}O_6NS$ , crystallises in hard lamellae, m. p. 108—109°. When the ester is dissolved in 10% sodium hydroxide solution, and kept for twenty-four hours, it



yields 3-cyano-2:4-diketotetrahydrothiophen,  $\text{S} \begin{smallmatrix} \text{CH}_2 & \text{C} & \text{OH} \\ & | & | \\ & \text{CO} & \text{C} & \text{CN} \end{smallmatrix}$ , which is probably formed by the rupture of the sulphur ring and its subsequent closing by the elimination of ethyl alcohol. The product crystallises with  $\text{H}_2\text{O}$ , has m. p.  $181-182^\circ$  (decomp.), is a monobasic acid, and hence has the keto-acolic constitution. The silver salt,  $\text{C}_4\text{H}_2\text{O}_2\text{NSAg}$ , is sparingly soluble, and the acid, which dissolves readily in most solvents, is best purified by conversion into its diacetyl derivative,  $\text{C}_{10}\text{H}_4\text{O}_4\text{NS}$ , which forms colourless needles, m. p.  $63-64^\circ$ .  
3-Cyano-2:4-diketotetrahydrothiophen,



obtained by condensing the ketone with benzaldehyde in the presence of sodium ethoxide, crystallises in pale yellow needles, m. p.  $220^\circ$  (decomp.), and forms a sodium salt,  $\text{C}_{12}\text{H}_6\text{O}_2\text{NSNa}$ , which separates as colourless crystals from alcohol. When boiled with excess of barium hydroxide solution for half an hour, the nitrile yields the bimolecular compound,  $\text{C}_{20}\text{H}_{12}\text{O}_5\text{N}_4\text{S}_4$ , as colourless needles, m. p.  $198^\circ$  (decomp.), after turning brown at  $180^\circ$ . It is sparingly soluble in water, and yields a barium salt,  $(\text{C}_{20}\text{H}_5\text{O}_4\text{N}_2\text{S}_2)_2\text{Ba}$ , as a colourless syrup which sets to a vitreous mass. When heated on the water-bath for a quarter of an hour with five times its weight of concentrated sulphuric acid, the nitrile takes up water and yields 2:4-diketotetrahydrothiophen.

3-carboxylamide,  $\text{S} \begin{smallmatrix} \text{CH}_2 & \text{C} & \text{OH} \\ & | & | \\ & \text{CO} & \text{C} & \text{CO} & \text{NH}_2 \end{smallmatrix}$ , which is deposited when the mixture is poured onto ice as a sparingly soluble, crystalline powder, m. p.  $177-178^\circ$  (decomp.). It yields a potassium salt,  $\text{C}_4\text{H}_2\text{O}_2\text{NSK}$ , which is sparingly soluble in alcohol. It has not been found possible to transform the nitrile or amide into the corresponding acid.

2-Imino-4-ketotetrahydrothiophen,  $\text{S} \begin{smallmatrix} \text{CH}_2 & \text{C} & \text{OH} \\ & | & | \\ & \text{C}(\text{NH}) & \text{CH} \end{smallmatrix}$ , obtained by heat-

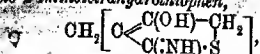
ing the ketonic ester with twenty times its weight of fuming hydrochloric acid, crystallises from water in colourless needles, which turn brown at  $190^\circ$ , and decompose at  $215^\circ$ . Its aqueous solution is neutral, but it dissolves in both alkalis and dilute acids. With a chloroform solution of bromine, it yields the 3-bromo-derivative,

$\text{S} \begin{smallmatrix} \text{CH}_2 & \text{C} & \text{OH} \\ & | & | \\ & \text{C}(\text{NH}) & \text{CBr} \end{smallmatrix}$ , which crystallises in brownish-coloured needles, m. p.  $157^\circ$ , and yields a hydrobromide. With nitrous acid it yields

the 3-oximino-derivative,  $\text{S} \begin{smallmatrix} \text{CH}_2 & \text{CO} \\ & | & | \\ & \text{C}(\text{NH}) & \text{C} & \text{N} & \text{OH} \end{smallmatrix}$ , as violet needles, decomposing at  $175^\circ$ , and when this is reduced with zinc dust and acetic

acid, 3-amino-2-imino-4-ketotetrahydrothiophen,  $\text{S} \begin{smallmatrix} \text{CH}_2 & \text{C} & \text{OH} \\ & | & | \\ & \text{C}(\text{NH}) & \text{C} & \text{NH}_2 \end{smallmatrix}$ , is obtained as plates, which turn brown at  $140^\circ$ , and are completely decomposed at  $174-175^\circ$ . The benzylidene derivative of the amine,  $\text{C}_{11}\text{H}_{10}\text{ON}_2\text{S}$ , decomposes at  $181^\circ$ . The amine reacts with nitrous acid, yielding an acid,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\text{S}$ , which decomposes at  $200^\circ$ , and forms a lead salt as a brown precipitate.

The imino-ketone reacts with warm formaldehyde solution, yielding methylenebis-4-keto-2-aminotetrahydrothiophen,

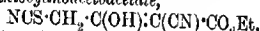


as colourless, soft, felted needles, which darken at 260°.

Ethyl thiobiscyanoacetoacetate crystallises from alcohol in glistening plates, m. p. 98—99°, and is the only product formed when hydrogen sulphide is passed into an alkaline solution of ethyl chlorocycanoacetoacetate. It yields a green precipitate with cupric acetate, is not hydrolysed by cold alkalis, but with concentrated sulphuric acid yields ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate and  $\alpha$ -carboxylamido-

lactic acid,  $\text{O} \begin{array}{l} \text{CH}_2 \cdot \text{C} \cdot \text{OH} \\ \text{CO} \cdot \text{C} \cdot \text{CO} \cdot \text{NH}_2 \end{array}$ , as colourless needles, m. p. 182—183° (decomp.).

Ethyl  $\alpha$ -cyano- $\gamma$ -thiocyanoacetoacetate,



obtained by the action of potassium thiocyanate on an alkaline solution of ethyl chlorocycanoacetoacetate, crystallises in slender needles, m. p. 82—84°. It decomposes when left exposed to the air, and when left in contact with fuming hydrochloric acid for twenty-four hours yields ethyl 2-imino-4-ketotetrahydrothiophen-3-carboxylate, but with cold concentrated sulphuric acid, it yields ethyl  $\alpha$ -cyano- $\gamma$ -thiocarbonylacetate,  $\text{NH}_2 \cdot \text{CO} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C(OH)} : \text{C(CN)} \cdot \text{CO}_2\text{Et}$ , as soft needles, m. p. 155—156°.

Practically all the compounds with the exception of the original 2-imino-4-ketotetrahydrothiophencarboxylate give deep red colorations with ferric chloride, and exist in the enolic forms given above.

J. J. S.

**Rotatory Power of Normal Quinine Hydrochloride.** ANDRÉ and LEULIER (*J. Pharm. Chim.*, 1910, [vii], 2, 23).—Experiments show that the specific rotatory power of normal quinine hydrochloride increases with the dilution, whereas the French Codex states diametrically the opposite, namely, that it increases with the concentration of the solution.

L. DE K.

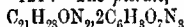
**Action of Chlorine and Ammonia on Quinine.** EZIO ROMANUCCI (Pamphlet 12 pp.).—By the action of chlorine or other oxidising agents followed by ammonia on salts of quinine, a number of coloured compounds are produced. In addition to the thalleioquinine  $\text{C}_{15}\text{H}_{20}\text{O}_5\text{N}_3$ , erythroquinine, rusioquinine ( $\text{C}_{21}\text{H}_{26}\text{O}_{10}\text{N}_3$ ), melanoquinine ( $\text{C}_{25}\text{H}_{36}\text{O}_{12}\text{N}_3$ ), and a colourless derivative previously known, the author has obtained a reddish-violet compound, rubroquinine, and a colourless substance, leucoquinine. From an examination of numerous quinine derivatives containing a phenolic hydroxyl group, the author comes to the conclusion that the production of these coloured substances depends on the presence of a phenolic group attached to a naphthalene or quinoline nucleus. Thalleioquinine is obtained as a green precipitate, m. p. 130°, by treating a quinine solution with chlorine water, and adding ammonia a few seconds

afterwards. On further treatment with chlorine water and ammonia, it yields a red substance, which contains chlorine. When the addition of ammonia is delayed about three times as long as in the case of thalleioquinine, and the ammonia added in two portions, rubroquinine is precipitated; it has m. p. 118—120°, is soluble in chlorine water, and is reprecipitated on adding ammonia. When a solution of quinine sulphate is treated with chlorine water for five minutes and then quickly with ammonia, a white precipitate, leucoquinine, is obtained. It has m. p. 138°, and is slightly soluble in chlorine water; on adding ammonia to the solution, a red precipitate is obtained. Rubroquinine and leucoquinine are soluble in acids.

R. V. S.

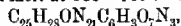
Constitution of Cinchonidine (Cinchotoxine). II. Derivatives and Salts of Ethyl-, Phenyl-, and  $\alpha$ -Naphthyl-cinchotoxol. EZIO COMANDUCCI (*Rend. R. Accad. Sci. Fis. Mat. Napoli*, 1910, Reprint 11 pp. Compare Abstr., 1909, i, 409).—By the preparation of the derivatives described in this paper, it is established that the vinyl group, and secondary and tertiary nitrogen atoms of cinchonidine are present also in the cinchotoxoles, whilst the ketonic group has been converted into a tertiary alcoholic grouping.

*Ethyl cinchotoxol hydrochloride*,  $C_{21}H_{25}ON_2 \cdot 2HCl$ , has m. p. 108—109° (sintering at 100°), and  $[\alpha]_D^{25} + 51.75^\circ$ . The *platinchloride*,  $C_{21}H_{25}ON_2 \cdot H_2PtCl_6 \cdot H_2O$ , is a red, crystalline powder, m. p. 210°. The *aurichloride*,  $C_{21}H_{25}ON_2 \cdot 2HAuCl_4 \cdot 3H_2O$ , a yellow, crystalline powder, has m. p. 120—121°. The *picrate*,

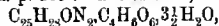


is prepared from the hydrochloride; it is a yellow powder, which sinters at 80°, and has m. p. 102°. When an insufficient quantity of picric acid is taken, a *picrate hydrochloride*,  $C_{21}H_{25}ON_2 \cdot HCl \cdot C_6H_3O_2N_3$ , m. p. 98°, is obtained. The *tartrate*,  $C_{21}H_{25}ON_2 \cdot C_4H_4O_6 \cdot H_2O$ , sinters at 95°, and melts at 107° (decomp.). The *methiodide*,  $C_{21}H_{25}ON_2 \cdot MeI$ , forms small, reddish-brown crystals, m. p. 138—140°. The *nitroso-derivative*,  $C_{21}H_{27}ON_2 \cdot NO$ , has m. p. 147—150° (decomp.); it gives Liebermann's reaction. The *benzoyl derivative*,  $C_{21}H_{25}ON_2 \cdot COPh$ , forms white, crystalline scales, m. p. 114°. The *bromine derivative*,  $C_{21}H_{25}ON_2 \cdot Br_2$ , is obtained by mixing chloroform solutions of bromine and the base; it is a reddish-white powder, m. p. 190° (sintering at 150°).

*Phenylcinchotoxol hydrochloride*,  $C_{18}H_{22}N_2 \cdot CPh \cdot OH \cdot 2HCl$ , sinters at 75°, and melts at 86—100°; it has  $[\alpha]_D^{25} + 21.09^\circ$ . The *platinchloride*,  $C_{25}H_{25}ON_2 \cdot H_2PtCl_6 \cdot H_2O$ , is a yellow powder, which decomposes above 200°. The *aurichloride*,  $C_{25}H_{25}ON_2 \cdot 2HAuCl_4$ , forms yellow tablets, which sinter at 70°, and melt at 113—115°. The *picrate*,

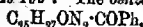


is a yellow powder, m. p. 105°. The *tartrate*,



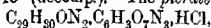
forms tablets or prisms, m. p. 225° (becoming brown at 180°); the anhydrous substance has m. p. 240°. The *methiodide*,  $C_{25}H_{25}ON_2 \cdot MeI$ , has m. p. 127—129° (sintering at 120°). The *nitroso-derivative*,  $C_{25}H_{27}ON_2 \cdot NO \cdot HCl$ , has m. p. 147—149°, and decomposes at 150°; it

gives Liebermann's reaction. The bromo-derivative,  $C_{25}H_{28}ON_2Br_2$ , sinters at  $150^\circ$  and melts at  $195^\circ$ . The benzoyl derivative,

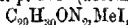


forms red scales, which sinter at  $165^\circ$ , and melt at  $178^\circ$  (decomp.). When phenylcinchotoxole is treated with a 2% solution of potassium permanganate at  $2^\circ$ , formic acid is produced, in addition to a yellow, crystalline substance of slightly acid reaction, which has m. p.  $188^\circ$  (becoming brown at  $167^\circ$ ).

$\alpha$ -Naphthylcinchotoxol hydrochloride,  $C_{18}H_{22}N_2 \cdot C(C_{10}H_7) \cdot OH \cdot 2HCl$ , is a deliquescent, reddish-brown mass, m. p.  $71-85^\circ$  (sintering at  $60^\circ$ ); it has  $[\alpha]_D^{25} + 49.6^\circ$ . The platinichloride,  $C_{29}H_{30}ON_2 \cdot H_2PtCl_6 \cdot H_2O$ , forms a yellow, amorphous powder, which becomes brown, and decomposes at  $330^\circ$ . The aurichloride,  $C_{29}H_{30}ON_2 \cdot 2HAuCl_4 \cdot H_2O$ , is a yellow powder, m. p.  $144-145^\circ$  (decomp.). The picrate hydrochloride,



sinters at  $97^\circ$ , and has m. p.  $101^\circ$  (decomp.). The methiodide,



is a reddish-brown substance, m. p.  $140^\circ$ .

R. V. S.

Constitution of Cinchonine (Cinchotoxins). III. Chloroethyl- and Chlorophenyl-cinchotoxile. EZIO COMANDUCCI (*Rend. R. Acad. Sci. Fis. Mat. Napoli*, 1910, Reprint 5 pp. Compare preceding abstract).—By the action of phosphoryl chloride and phosphorus pentachloride in chloroform solution, the alcoholic hydroxyl group of the R-cinchotoxols (compare Abstr., 1909, i, 409) may be replaced by chlorine; the substances so obtained are termed by the author chloro-R-cinchotoxiles.

Chloroethylcinchotoxile,  $C_{18}H_{21}N_2 \cdot C_2H_4Cl$ , is a reddish-brown powder, which sinters at  $85^\circ$ , and melts at  $115-117^\circ$ . The platinichloride,  $C_{21}H_{20}N_2Cl_2 \cdot H_2PtCl_6$ , forms a reddish-yellow powder, which becomes brown at  $210^\circ$ . The picrate,  $C_{21}H_{20}N_2Cl_2 \cdot C_6H_3O_7N_3$ , is a yellow powder, which becomes brown at  $115^\circ$ , and melts at  $130^\circ$ .

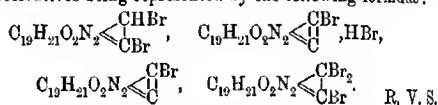
Chlorophenylcinchotoxile forms dark yellow scales, m. p.  $148-155^\circ$ . The platinichloride,  $C_{26}H_{23}N_2Cl_2 \cdot H_2PtCl_6$ , becomes brown, and decomposes at  $220^\circ$ . The picrate,  $C_{26}H_{23}N_2Cl_2 \cdot C_6H_3O_7N_3$ , has m. p.  $121-122^\circ$ . By the action of alcoholic potassium hydroxide on the chlorophenyl-derivative, a compound was obtained, which had m. p.  $62-63^\circ$ , and was free from chlorine.

R. V. S.

Strychnine and Brucine. ROBERTO CIUSA and G. SCAOLJARIANI (*Atti R. Acad. Lincei*, 1910, [v], 19, i, 555-561. Compare Beckurts, Abstr., 1905, i, 918, and Martin, Abstr., 1904, i, 446).—By the action of bromine on a solution of strychnine in glacial acetic acid, a di-bromide,  $C_{21}H_{22}O_2N_2Br_2$ , is produced. The substance crystallises from alcohol in rosettes of colourless needles, m. p.  $122^\circ$ , but by repeated crystallisation from alcohol, or by heating above its m. p., it is converted into another, more stable form, which forms large, colourless, monoclinic crystals, m. p.  $260^\circ$ . In the preparation of the dibromide the formation of a perbromide,  $C_{21}H_{22}O_2N_2Br_3$ , may occur. When the dibromide is boiled with water, it dissolves, and the solution on cooling

deposits the *hydrobromide* of the monobromostrychnine, m. p. 222°, of Beckurts (*loc. cit.*) and Martin (*loc. cit.*). This monobromostrychnine does not lose bromine even when heated with alcoholic potassium hydroxide in a sealed tube. With chloroanil in ethereal-alcoholic solution it gives a violet coloration, and with concentrated sulphuric acid and potassium dibromate it yields a fugitive, reddish-violet coloration. When it is treated with bromine, a *perbromide*,  $C_{21}H_{21}O_2N_2Br_6H_2O$ , is formed, which crystallises in golden-yellow needles, which on heating darken at 200° with loss of bromine. On heating this compound with water or with thiosulphate solution, a *substance* is obtained containing 28.35–28.49% bromine. From the methyl-alcoholic mother liquors of the perbromide, a crystalline *hydrobromide* of the composition  $C_{21}H_{21}O_2N_2Br_2 \cdot HBr \cdot H_2O$  can be obtained. From the mother liquor of this substance the addition of potassium hydroxide precipitates the *dibromide* of monobromostrychnine; it could not be crystallised.

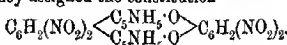
Whilst strychnine and monobromostrychnine reduce acid solutions of permanganate at once, the dibromides of these substances only do so after a time. Monobromostrychnine and the two dibromides do not react with hydroxylamine or with *p*-nitrophenylhydrazine. The authors consider that the above behaviour may be explained by the presence of the grouping  $X \begin{smallmatrix} \text{CH} \\ | \\ \text{C} \end{smallmatrix}$  in strychnine, the constitutions of the above derivatives being represented by the following formulae:




**Amine Peroxides of Brucine and Strychnine.** GUSTAV MOSSLER (*Monatsh.*, 1910, 31, 329–345).—When brucine is heated with 3% hydrogen peroxide on the water-bath and the solution is concentrated in a vacuum, crystals of a *peroxide* containing two atoms of active oxygen are obtained, which contain 4H<sub>2</sub>O when slowly crystallised, 3H<sub>2</sub>O when rapidly crystallised, and 2H<sub>2</sub>O when dried in a vacuum. Another mol. of H<sub>2</sub>O can be expelled at 100° or by crystallisation from alcohol, but the elimination of the remaining H<sub>2</sub>O is accompanied by the loss of the active oxygen. The peroxide has m. p. 202–203° (decomp.), the air-dried crystals softening at 115–125°, those dried in a vacuum at 135°. In aqueous solution the peroxide dissociates into brucine oxide and hydrogen peroxide, but it dissolves without decomposition in non-dissociating solvents, alcohol, or chloroform. An aqueous solution, warmed with platinum black, evolves oxygen and yields brucine oxide, which can be reconverted into the peroxide by hydrogen peroxide. In 3% hydrogen peroxide the substance has  $[\alpha]_D -5.12^\circ$ , and yields with dilute sulphuric acid mainly the sulphate of brucine oxide. Sulphurous acid eliminates the active oxygen from the peroxide, leaving a mixture of brucine and *allo-brucine*. *Strychnine peroxide* is obtained with some difficulty from strychnine and 14% hydrogen peroxide. The air-dried crystals contain 4H<sub>2</sub>O, two

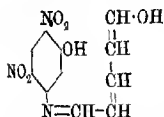
which are lost in a vacuum, the substance then having m. p. 178° (decomp.), and containing two atoms of active oxygen. The peroxide is almost completely dissociated in aqueous solution. In 95% alcohol it has [α]<sub>D</sub><sup>20</sup> - 7°. C. S.

Action of Pyridine on 1:3-Dichloro-4:6-dinitrobenzene.  
 FREDERICK ZIRCKE and G. WEISPFENNING (*J. pr. Chem.*, 1910, [ii], 82,  
 [1-17].—By the action of hot pyridine on 1:3-dichloro-4:6-dinitro-  
 benzene, Reitzenstein and Rothschild (Abstr., 1906, 1,  
 454) obtained, together with dinitrophenyldi-  
 pyridinium dichloride, a yellow condensation product, to  
 which they assigned the constitution

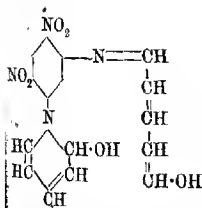


 This substance is now shown to be a betaine anhydride (annexed constitution), produced from the dinitrophenyldipyridinium dichloride by the action of the water present. It can also be prepared by the action of sodium nitrite on an aqueous solution of the dichloride, and by heating pyridine and 3-chloro-4:6-dinitrophenol at 100°. The addition of alcohol to solutions of the substance in moderately concentrated acids precipitates well characterised salts, of which the *chloride*, *chromate*, *platinichloride*, *nitrate*, and *sulphate* are described. It is converted into pyridine and dinitroresorcinol by 20% hydrochloric acid at 170°, and into pyridine and chlorodinitrophenol by hydrogen chloride in glacial acetic acid at 150°.

The action of excess of 2*N*-sodium hydroxide on an aqueous solution of the chloride of the condensation product yields a red substance,  $C_{11}H_9O_2N_3$ , which has not the constitution given to it by



nitro-3-aminophenol, and by hot aniline, yielding the dinitroamino-phenol and the dianilide,  $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NHPh}$ , previously described.



Dinitrophenyldipyridinium dichloride forms colourless prisms containing  $2\text{H}_2\text{O}$ , which decompose by heating, pyridine, hydrogen chloride, and the yellow anhydride being produced. An aqueous solution, by treatment with sodium carbonate, or, better, with ammonium hydroxide, becomes violet, and finally deposits a blackish-green precipitate of a substance,  $\text{C}_{10}\text{H}_4\text{O}_6\text{N}_4$ , which forms red salts (the chloride, platinichloride, bromide), and receives the annexed constitution,

one pyridine ring being ruptured and the other converted into the  $\beta$  form. The substance yields the yellow betaine anhydride by treatment with boiling glacial acetic acid and acetic anhydride, and is decomposed by boiling 2*N*-hydrochloric acid, yielding 4:6-dinitro-3-amino-phenylpyridinium chloride,  $C_{11}H_6O_4N_4Cl$ , m. p. 230–235° (decomp.). The blackish-green substance is also decomposed by aniline, yielding dinitrodiaminobenzene and the dianilide mentioned above. C. S.

**Quinoline Sulphosalicylate.** GEORGES PRUNIER (*J. Pharm. Chim.*, 1910, [vii], 1, 538–539).—*Quinoline sulphosalicylate*,  $HSO_3 \cdot C_6H_4(OH) \cdot CO_2H \cdot C_8H_7N \cdot H_2O$ ,

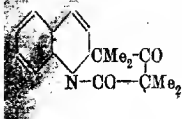
obtained by the action of the acid on the base in presence of water, melts partly at 110° and becomes anhydrous, and then melts at 220°. It crystallises in colourless, silky tufts, is sparingly soluble in cold water (1.547 parts per 100 at 17°), more so in warm water or alcohol, and is acid in reaction. It is poisonous in doses of 0.29 to 0.34 gram per kilogram of body-weight when applied subcutaneously or intravenously. Its antiseptic power is about the same as that of phenol, and its bactericidal action somewhat less. Its reactions with a number of common reagents are tabulated. T. A. H.

**Ketens. II. Dimethylketen Bases.** HERMANN STAEDINGER, HELMUT W. KLEVER, and P. KOBER (*Annalen*, 1910, 374, 1–38. Compare Abstr., 1907, i, 424; 1908, i, 318).—An investigation of the keten bases formed by the combination of dimethylketen with tertiary bases.

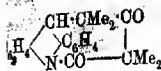
The dimethylketen bases, as a general rule, when treated with dilute mineral acids or alkalis, unite with a molecule of water, yielding acids having the composition 1 mol. base + 1 mol. keten + 1 mol. water or 1 mol. base + 1 mol. keten + 1 mol. isobutyric acid respectively. The corresponding esters and anilides of the acids may be obtained by acting on the keten base with an alcohol or aniline. The acids are converted by hot strong mineral acids into 2 mols. of isobutyric acid and 1 mol. of the tertiary base, and decompose when heated at a high temperature; for example, dimethylketenquinoline decomposes into quinoline and isobutyric anhydride.

The reactivities of the dimethylketen bases and of the acids derived from them varies with the nature of the tertiary base; thus, the pyridine compounds are very unstable, the derivatives of the quinoline series less reactive, whilst keten-acridine is so stable that it does not yield an acid, neither is it possible to decompose it with the formation of acridine and isobutyric acid.

Although the several reactions of dimethylketenquinoline may be satisfactorily accounted for by means of the constitutional formula advanced in a previous paper (compare Abstr., 1907, i, 424), nevertheless this formula is shown to be incorrect and must be replaced by the annexed formula, for it is found that Schiff's bases combine with 2 mols. of keten, the combination taking place through the C:N-linking. It is for this reason that only tertiary bases containing the C:N-group combine with dimethylketen; in the case of



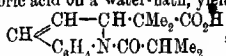
bridge, it is probable that the formation of the keten base results through the fission of the para-linking, the base having the annexed formula. Generally speaking, Schiff's bases



combine with dimethylketen, yielding  $\beta$ -lactams, which undergo further change into  $\beta$ -amino acids; benzylidenbenzylamine, however, in addition to the normal  $\beta$ -lactam, yields two other substances having the composition 1 mol. of Schiff's base + 2 mols. of dimethylketen, of which one, the chief product of the reaction, possesses the same characteristics as the dimethylketen bases already discussed. It is shown that this substance is 2:4-diketo-6-phenylbenzyl-3:3:5:5-tetramethylpiperidine, since the acid formed by the action of a dilute solution of sodium carbonate on the keten base is identical with the substance obtained by treating the corresponding ester of  $\beta$ -benzylamino- $\beta$ -phenyl- $\alpha\alpha$ -dimethylpropionic acid with isobutyric anhydride.

Benzylidenemethylamine, in analogy to benzylidenbenzylamine, reacts with dimethylketen, yielding as chief product a keten base.

Dimethylketenquinoline (compare Abstr., 1907, i, 424), when heated with dilute hydrochloric acid on a water-bath, yields an acid,

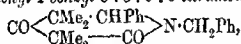


which forms a colourless, compact crystals, m. p. 152–153°; many derivatives of the acid have been described previously (*loc. cit.*).

Dimethylketen- $\beta$ -naphthaquinoline,  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}$ , forms white crystals, m. p. 165°; the acid derived from it,  $\text{C}_{21}\text{H}_{21}\text{O}_3\text{N}$ , crystallises in white needles, m. p. 171°.

Dimethylketenisoquinoline,  $\text{C}_{17}\text{H}_{19}\text{O}_2\text{N}$ , crystallises in leaflets and needles, m. p. 105°; it gives rise to an acid,  $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ , which forms white crystals, m. p. 138°. The acid,  $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}$ , derived from dimethylketenpyridine, crystallises in large, colourless, prisms, m. p. 94–95°.

2:4-Diketo-6-phenyl-1-benzyl-3:3:5:5-tetramethylpiperidine,



prepared from dimethylketen and benzylidenbenzylamine, could not be isolated in a pure state; it is converted by a hot aqueous solution of sodium carbonate chiefly into  $\beta$ -isobutyrylbenzylamino- $\beta$ -phenyl- $\alpha\alpha$ -dimethylpropionic acid,  $\text{CHMe}_2 \cdot \text{CO} \cdot \text{N}(\text{CH}_2\text{Ph}) \cdot \text{CHPh} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{H}$ , which forms colourless crystals, m. p. 169.5° (decomp.); the silver salt is a crystalline, white powder. The acid is decomposed by boiling concentrated hydrochloric acid, yielding benzylamine,  $\beta$ -benzylamino- $\beta$ -phenyl- $\alpha\alpha$ -dimethylpropionic acid, isobutyric acid, benzaldehyde, dimethylstyrene, and benzylbutyramide,  $\text{C}_{11}\text{H}_{15}\text{ON}$ , white leaflets, m. p. 92°. Oxidation of the acid by potassium permanganate leads to the formation of isobutyric acid, benzoic acid, and a substance,  $\text{C}_{22}\text{H}_{23}\text{O}_3\text{N}$ , obtained as a white, crystalline powder, m. p. 195°. The following derivatives of the acid were prepared either from the acid or from the keten base by the usual methods: methyl ester,  $\text{C}_{23}\text{H}_{25}\text{O}_3\text{N}$ , large, colourless prisms, m. p. 109°; ethyl ester,  $\text{C}_{24}\text{H}_{27}\text{O}_3\text{N}$ , m. p. 111–112°; bromide, an amorphous powder which could not be



phenylhydrazide,  $C_{28}H_{23}O_2N_4$ , a white, crystalline powder, m. p. 138°; phenylhydrazide,  $C_{28}H_{23}O_2N_4$ , colourless, felted needles, m. p. 155°.

The lactam of  $\beta$ -benzylamino- $\beta$ -phenyl- $\alpha$ -dimethylpropionic acid,  $OMe_2 \left\langle \begin{array}{c} CHPh \\ CO \end{array} \right\rangle N \cdot CH_2Ph$ , is formed; together with isobutyric acid, by heating the acid just described at 180°; it forms large, white prisms, m. p. 36°, and is not altered by a hot alcoholic solution of phenylhydrazine or hydroxylamine, but is converted by an alcoholic solution of potassium hydroxide into the salt of the corresponding acid; the solution of the potassium salt thus obtained, when acidified with acids, yields the corresponding salts; the acetate,  $C_{18}H_{21}O_2N, Me \cdot CO_2H$ , is a white, crystalline powder, m. p. 190—191° (decomp.); the hydrochloride,  $C_{18}H_{21}O_2N, HCl$ , forms crystalline nodules, m. p. 142°. The amino-acid is obtained by dissolving the acetate in a known excess of aqueous sodium hydroxide, and adding the requisite quantity of hydrochloric acid; it crystallises with  $1H_2O$  in small, white needles, m. p. 138—142°; the anhydrous substance has m. p. 145—148°; the ethyl ester,  $C_{20}H_{25}O_2N$ , prepared from the silver salt and ethyl iodide, has m. p. 63—64°. Attempts to replace the hydrogen of the  $NH_2$  group by the isobutyryl group by heating the acid with isobutyryl chloride led to the formation of the  $\beta$ -lactam. The isobutyryl group can be introduced, however, by heating the ethyl ester with isobutyric anhydride.

The formation of 2:4-diketo-6-phenyl-1-benzyl-3:3:5:5-tetramethylpiperidine from dimethylketen and benzylidenemethylamine is accompanied by the formation of the  $\beta$ -lactam just described, together with a substance,  $C_{22}H_{25}O_2N$ , m. p. 117°, which is extremely stable towards acids and alkalis.

Dimethylketen-benzylidenemethylamine, 2:4-diketo-6-phenyl-1:3:3:5:5-pentamethylpiperidine, prepared from dimethylketen and benzylidenemethylamine, could not be obtained pure; when heated with an aqueous solution of sodium carbonate, it yields the corresponding acid,  $C_{18}H_{23}O_2N$ , a white, crystalline powder, m. p. 142° with evolution of isobutyric acid; the methyl ester,  $C_{17}H_{23}O_2N$ , crystallises in white needles, m. p. 78°. The acid, when heated at 150°, yields the lactam of  $\beta$ -methylamino- $\beta$ -phenyl- $\alpha$ -dimethylpropionic acid,  $C_{12}H_{15}ON$ , an oil, b. p. 139.5°/13 mm.; the corresponding acid,  $C_{12}H_{17}O_2N$ , is obtained as a crystalline powder, m. p. 260°, which is possibly an internal ammonium salt. A substance,  $C_{19}H_{21}O_2N$ , is formed as a by-product in the interaction of dimethylketen and benzylidenemethylamine; it forms crystals, m. p. 115°.

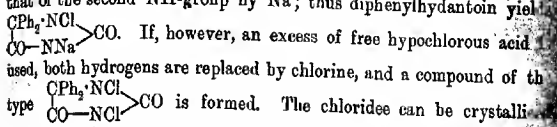
W. H. G.

Researches on Benzidine Formation. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 527—538).—A résumé of results already published, in part, in *Abstr.*, 1905, i, 651; 1906, i, 314; 1909, i, 741. The following new compounds are described: 2:2'-Dinitro-4:4'-diacetylaminodiphenylmethane,  $CH_3[C_6H_4(NO_2)_2 \cdot NH_2]_2$ , m. p. 239°, forms yellow crystals, and on reduction with stannous chloride yields the corresponding 2:2'-diamino-compound, m. p. 244°, which crystallises in colourless needles from dilute alcohol.

4:4'-Tetramethyldiamino-2:2'-azodiphenylmethane, on reduction

with stannous chloride in hydrochloric acid, furnishes 4:4-tetramethyldiamino-2:2-diaminodiphenylmethane (Pinnow, Abstr., 1896, i, 98), and this on further reduction with zinc dust and sodium hydroxide gives 4:4-tetramethyldiaminoacridine (Biehringer, Abstr., 1897, i, 73). T. A. H.

**Action of Hypochlorous Acid and of Sodium Hypochlorite on Hydantoin and Acetylenediureine.** HEINRICH BILTZ and OTTO BEHRENS (*Ber.*, 1910, 43, 1984—1996. Compare Abstr., 1909, i, 848).—Sodium hypochlorite reacts with hydantoins and acetylenediureines, so that the H of one NH-group becomes replaced by Cl, and that of the second NH-group by Na; thus diphenylhydantoin yields



**1:3-Dichloro-5:5-diphenylhydantoin,**  $\begin{array}{c} \text{CPh}_2\text{NCl} \\ \diagup \\ \text{CO}-\text{NCl} \end{array} > \text{CO}$ , crystallises in well-developed, six-sided prisms, m. p. 164° (decomp.). It crystallises from benzene with  $\frac{1}{2}\text{C}_6\text{H}_6$ , which it loses at 108°. When methylated by means of methyl sulphate and dilute alkali, it yields 5:5-diphenyl-1:3-dimethylhydantoin (Biltz and Rimpel, Abstr., 1908, i, 462).

**1-Chloro-5:5-diphenyl-3-methylhydantoin,**  $\begin{array}{c} \text{CPh}_2\text{NCl} \\ \diagup \\ \text{CO}-\text{NMe} \end{array} > \text{CO}$ , prepared by the action of sodium hypochlorite on 5:5-diphenyl-3-methylhydantoin, crystallises in prisms, m. p. 186° (decomp.).

**1:3-Dichloro-5:5-dibromophenylhydantoin,**  $\begin{array}{c} (\text{C}_6\text{H}_4\text{Br})_2\text{C}-\text{NCl} \\ \diagup \\ \text{CO}-\text{NCl} \end{array} > \text{CO}$ , crystallises in rhombic plates, m. p. 241° (decomp.), and can be readily methylated, and yields the same 5:5-dibromophenyl-1:3-dimethylhydantoin,  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2\text{Br}_2$ , m. p. 199°, as is obtained by methylating di-5-bromophenylhydantoin itself, or by condensing dibromobenzil with dimethylcarbamide at 210°.

**4:5-Dibromophenyl-1:3-dimethylglyoxalono-4:5-glycol,**

$$\begin{array}{c} \text{C}_6\text{H}_3\text{Br}_2\text{C}(\text{OH})\cdot\text{NMe} \\ \diagup \\ \text{C}_6\text{H}_3\text{Br}_2\text{C}(\text{OH})\cdot\text{NMe} \end{array} > \text{CO},$$

obtained by boiling a mixture of dibromobenzil and s-dimethylcarbamide with sodium ethoxide solution for two hours, crystallises in rhombic plates, m. p. 212°. When heated at its m. p., it loses water and yields 5:5-dibromophenyl-1:3-dimethylhydantoin.

5:5-Dibromophenyl-5-methylglyoxalane,  $(C_6H_4Br)_2C(NH)CO-NMe$ , is obtained by boiling dibromobenzil and methylearhamide with an alcoholic solution of sodium ethoxide for three hours, and crystallises in rhombic plates or prisms, m. p. 267°.

1-Chloro-5:5-dibromophenylhydantoin,  $(C_6H_4Br)_2C(NH)CO-NH$ , obtained by the action of carbon dioxide on its sodium derivative, crystallises in compact rhombohedra, m. p. 203° (decomp.). When diphenylthiohydantoin is treated with sodium hypochlorite and then with carbon dioxide, diphenyldichlorohydantoin is obtained.

1:3:7:9-Tetrachloro-4:5-diphenylacetylenediureine,  $CO \begin{matrix} NCl-CPh-NCl \\ NCl-CPh-NCl \end{matrix} CO$ , crystallises in six-edged prisms, m. p. 249° (decomp.).

1-Chloro-3-sodium-4:5-diphenylacetylenediureine,  $CO \begin{matrix} NCl-CPh-NH \\ NNa-CPh-NH \end{matrix} CO$ , crystallises in long, glistening prisms, and, when carbon dioxide is passed into its aqueous solution, yields 1-chloro-4:5-diphenylacetylenediureine,  $C_{16}H_{13}O_2N_2Cl$ , which crystallises from acetone in six-sided prisms, m. p. 218° (decomp.).

Acetylenediureine is not so stable towards sodium hypochlorite, and at 95° yields 30% of free nitrogen. 4:5-Dimethylacetylenediureine behaves in a similar manner. J. J. S.

**Catalytic Racemisation of Optically Active Hydantoin Derivatives and of Related Substances as the Result of Tautomeric Change.** HENRY D. DAKIN (*Amer. Chem. J.*, 1910, 44, 48—60).—In *N*-sodium hydroxide the rotation of the active hydantoins,

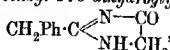
$$CHR \begin{matrix} NH \cdot CO \\ CO \cdot NH \end{matrix}$$
  
(where R is  $\cdot CH_2Pr^s$ ,  $p\text{-OH}\cdot C_6H_4\cdot CH_2\cdot$ ,  $\cdot CH_2\cdot CO_2H$ , or  $\cdot CH_2\cdot CH_2\cdot CO_2H$ ),

diminishes to zero in the course of many hours, the solutions then yielding the *i*-hydantoins by acidification. The rotation of the corresponding carhamido-acids remains constant in *N*-sodium hydroxide. The loss of activity of the hydantoins is most obviously explicable by enol-keto-desmotropy,  $CH \cdot CO \rightleftharpoons C \cdot C \cdot OH$  (compare Wren, *Trans.*, 1909, 95, 1593), the correctness of the explanation being supported by the case of the hydantoin,  $CMeEt \begin{matrix} NH \cdot CO \\ CO \cdot NH \end{matrix}$ , obtained from crovaline, the rotation of which remains constant in *N*-sodium hydroxide.

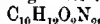
The following new compounds have been obtained by evaporating active amino-acids with aqueous potassium cyanate, and boiling the resulting active hydantoic acids with 10% hydrochloric acid: *D*-iso-butylhydantoinic acid, m. p. 205—206° (decomp.),  $[\alpha]_D^{25}$  1.9° in *N*-sodium hydroxide ( $\epsilon = 3.15$ ), from *L*-leucine; *l*-isobutylhydantoin, m. p. 212°.

$[\alpha]_D^{20} - 68.2$  in  $\gamma$ -sodium hydroxide ( $c = 1.925$ ), becoming 0° after thirty hours; *d*-methylethyldantoin, m. p. 172–173°,  $[\alpha]_D^{20} 32.2$  ( $c = 1.247$ ), from *l*-isovaline. C. S.

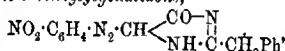
**Two Isomeric Benzylglyoxalidones.** HERMANN FINGER and W. ZEH (*J. pr. Chem.*, 1910, [ii], 82, 50–60).—Two isomeric benzylglyoxalidones are obtained when benzyliminoethyl ether is employed in the reaction described previously (Abstr., 1906, i, 901; 1907, i, 876). 4-Keto-2-benzyl-4:5-dihydroglyoxaline,



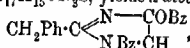
m. p. 143°, obtained by keeping the imino-ether and ethyl glycine at 20° for two hours, is a weak monoacidic base. It is decomposed by hydrochloric acid, D 1.12, at 130° into phenylacetic acid, glycine, and ammonia, reacts with boiling water to form a substance,



m. p. 176–177°, which is probably phenylacetyl-glycinamide, forms with *p*-nitrodiazobenzene chloride in the presence of sodium acetate 5-*p*-nitrobenzenazo-2-benzylglyoxalidone,

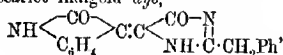


yellow needles, darkening at 235°, combines with phenylcarbimide to form a phenylcarbamide,  $\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_3$ , with phenylthiocarbimide to form a phenylthiocarbimide,  $\text{C}_{17}\text{H}_{13}\text{ON}_3\text{S}$ , yields a dibenzoyl derivative,



m. p. 138°, with benzoyl chloride in pyridine, benziminylbenzylglyoxalidone,  $\text{NH}\cdot\text{CPh}\cdot\text{N}\begin{array}{l} \text{CH}_2-\text{CO} \\ \text{C}(\text{CH}_2\text{Ph})\cdot\text{N} \end{array}$ , sulphur-yellow leaflets,

m. p. 237°, with benzyliminoethyl ether, 5-benzyl-2-benzylideneglyoxalidone, m. p. 177.5°, with benzaldehyde in faintly alkaline solution, condenses with diacetyl to form a reddish-orange substance,  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2$ , decomposing at 196°, and reacts with isatin in hot glacial acetic acid to form a scarlet indigoid dye,



which is reduced by alkaline bysopulphite to a yellowish vat-dye, oxidising rapidly in air.

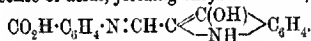
The isomeric substance, isobenzylglyoxalidone,  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$ , m. p. 222° (decomp.), which is the chief product of the reaction when benzyliminoethyl ether and ethyl glycine are heated together, is probably the cyclic amidine,  $\text{CH}_2\text{Ph}\cdot\text{C}\begin{array}{l} \text{N}-\text{CH}_2 \\ \text{NH}\cdot\text{CO} \end{array}$ . It is not attacked

by boiling water, yields phenylacetic acid, glycine, and ammonia when decomposed by hydrochloric acid at 140°, forms an acetyl derivative, m. p. 189° (not sharp), with acetic anhydride, gives successively yellow, greenish-blue, reddish-violet, and red colorations when heated with glacial acetic acid, and yields a substance,  $\text{C}_{13}\text{H}_{16}\text{O}_2\text{N}_2$ , by heating with sodium hydroxide and subsequent acidification.

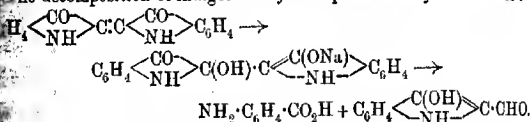
C. S.

**Decomposition of indigotin and of indirubin by Alkalies.** PAUL FEINBLÄNDER and KARL SCHWENK (*Ber.*, 1910, 43, 1971—1975. Compare Fritzsche, *Annalen*, 184K, 39, 79; Heumann and Bachofen, *Ber.*, 1893, i, 270; Hentschel, *ibid.*, 1900, i, 231).—The decomposition of indigotin by alkalis cannot take place according to the equation given by Henschel, as the amount of indoxyl is very small, and varies with the temperature and the length of time of heating. The indoxyl is a secondary decomposition product. Fritzsche's chrysanthic acid is not a primary decomposition product; it is formed by the condensing action of the added acid on anthranilic acid and indoxyl-2-aldehyde, both of which are present as potassium salts after the fusion. The two are separated by taking the dilute solution of the fused mass, freeing it from indoxyl, and pouring into cold dilute hydrochloric acid, which is continually stirred, and also covered with a layer of ether. The anthranilic acid is then present in the aqueous, and the aldehyde in the ethereal, solution.

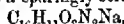
**Indoxyl-2-aldehyde**,  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CHO}$ , crystallises from warm water or from a mixture of chloroform and light petroleum in glistening needles, which decompose at about  $160^\circ$ . It condenses with anthranilic acid in the presence of acids, yielding chrysanthic acid,



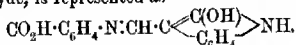
The decomposition of indigotin may be represented by the scheme:



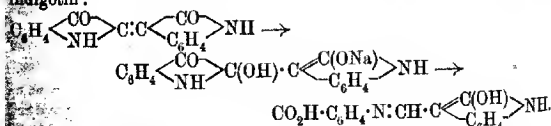
When indirubin is heated with concentrated sodium hydroxide at  $150^\circ$ , it is transformed into a sparingly soluble sodium salt,



from which acids liberate the acid,  $C_{10}H_{11}O_5N_2$ . This crystallises from nitrobenzene in long, glistening, yellow needles, m. p. above  $256^\circ$ . When heated at  $150^\circ$ , it yields carbon dioxide, aniline, and oxindole, and as it can be synthesised from anthranilic acid and oxindole-3-aldehyde, is represented as



The action of alkali on indirubin is thus analogous to its action on indigotin:



**Oxindole-3-aldehyde**,  $C_6H_4 \begin{smallmatrix} \text{C(CHO)} \\ \text{NH} \end{smallmatrix} C \cdot \text{OH}$ , is prepared readily by the action of alkalis on thioindigo-scarlet (3'-indoxyl-2-thionaphthen-

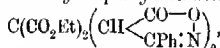
zone: 1. white, 2. yellow, 3. red, 4. black, 5. 675, the other products being *o*-thiolbenzoic acid. The aldehyde crystallises from dilute alcohol in pale yellow needles, m. p. 213°, and is more stable than indoxyl-2-aldehyde. J. J. S.

**Condition of Indigo-White in Aqueous Solutions.** EDUARD KNECHT and J. P. BATEY (*J. Soc. Dyers*, 1910, 28, 171—173).—Calcium indigo-white has been shown by the boiling-point method to be crystalloid in solution. A solution of purified monosodium indigo-white is found to be an electrolyte. The material was prepared by mixing alcoholic sodium hydroxide with an excess of alcoholic indigo-white in an atmosphere of hydrogen, evaporating to dryness, and treating the residue with air-free water for two and a-half hours. The indigo-white in the solution, determined by oxidation and direct weighing, was very slightly in excess of the proportion required for pure monosodium salt.

The molecular conductivity of monosodium indigo-white is 62.6 at 19.35 litres and 67.7 at 37.85 litres dilution, that is, about 2/3 the conductivity of sodium chloride.

Cotton adsorbs indigo-white and sodium hydroxide in approximately equivalent proportions from a solution of monosodium salt, but more indigo and more alkali are adsorbed in presence of excess of sodium hydroxide. No definite relation between the amounts of indigo and alkali taken up in these cases could be found, but as nearly all the indigo can be washed out with air-free water, the action is doubtless an adsorption by the cotton. R. J. C.

**Condensation of Phenylisooxazolone with Ethyl Mesoxalate.** ANDRÉ MEYER (*Compt. rend.*, 1910, 150, 1765—1767. Compare *Abstr.*, 1908, i, 368).—When an alcoholic solution of ethyl mesoxalate (1.1 mol.) is boiled for thirty minutes with phenylisooxazolone, a good yield of *ethyl bisphenylisooxazolone mesoxalate*,



is obtained. This compound crystallises in large octahedra, m. p. 187° (decomp.), and forms solutions in aqueous alkali hydroxides or carbonates, from which it is precipitated by the addition of mineral acids. The sodium salt,  $C_{25}H_{20}O_8N_2Na_2$ , occurs in hexagonal crystals; its aqueous solution gives a violet precipitate with ferric chloride; the silver, lead, mercuric, and zinc salts are insoluble. The diethyl derivative,  $C_{25}H_{20}O_8N_2$ , obtained by the action of ethyl iodide on the sodium salt, crystallises in slender needles, m. p. 200—201°. The diacetyl derivative forms prisms, m. p. 166°; the dibenzoyl derivative has m. p. 194°.

The addition of benzenediazonium chloride to a solution of the compound in alkali results in the formation of Claisen's benzeneazophenylisooxazolone (*Abstr.*, 1891, 468). W. O. W.

**Action of Hydrazoic Acid on Some Acids of the Acetylene Series. Synthesis of Derivatives of 1:2:3-Triazole.** E. OLIVERI-MANDALÀ and A. COPPOLA (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 563—569. Compare Oliveri, *ibid.*, 1905, [v], 14, i, 228).—When an

an ethereal solution of acetylenedicarboxylic acid (Perkin, *Trans.*, 1907, 91, 834) is warmed for a short time with an ethereal solution of hydrazoic acid, 1:2:3-triazoledicarboxylic acid, identical with that of Bladin and of Zincke (*Abstr.*, 1896, i, 550), is obtained. This substance yields with 3 molecules of diazomethane a *trimethyl* derivative, m. p. 55–60°, in which one of the methyl groups is attached to nitrogen, since it yields methylamine when boiled with concentrated alkali. Phenylpropionic acid and hydrazoic acid react but slowly, only 7/10 of the substances having condensed after six days at 45–50°. The behaviour of this acid with hydrochloric acid is similar (Michael and Pendleton, *Abstr.*, 1889, 1063). The product, 4-phenyl-1:2:3-triazole-5-carboxylic acid, has m. p. 205–206°, decomposing into carbon dioxide and phenyltriazole. Analysis indicated the presence of  $\frac{1}{2}$ H<sub>2</sub>O, but it was not possible to eliminate this from the substance. The barium salt crystallises with 2H<sub>2</sub>O. 4-Phenyl-1:2:3-triazole, obtained by heating the above acid at 210–215°, has m. p. 143–145°, and displays both basic and acid properties; it yields a *silver* salt, dissolves in dilute alkalis, and is precipitated again by acids; it forms a *hydrochloride*, m. p. about 140°, and a *platinichloride*. 1:2:3-Triazolecarboxylic acid (Dimroth, *Abstr.*, 1902, i, 403) can be prepared similarly. R. V. S.

**Decomposition of Certain Cyclic Imines by means of Sodium Hypochlorite** HEINRICH BILTZ and OTTO BEHRENS (*Ber.*, 1910, 43, 1996–1999).—Allantoin, 3-methylallantoin, 5-hydroxy-1:3-dimethylhydantoincarbamide (Biltz, this vol., i, 521), 7:9-dimethyluric acid glycol, and parabanic acid give almost theoretical amounts of nitrogen at the ordinary temperature in the presence of sodium hypochlorite solution and excess of potassium hydroxide. Uric acid and its methyl derivatives under similar conditions evolve nitrogen slowly, and in most cases the amount of nitrogen corresponds with the non-methylated imino-groups present. An exception is 7-methyluric acid.

Alloxan also reacts but slowly with hypochlorite. Methyl- and dimethyl-carbamides react only slowly with hypochlorite. J. J. S.

**Methylation and Constitution of Allantoin.** HEINRICH BILTZ (*Ber.*, 1910, 43, 1999–2003. Compare Siemonsen, *Abstr.*, 1904, i, 951).—3-Methylallantoin can be prepared by the action of methyl iodide on the silver salt of allantoin. Although the yield is only 33% of the theoretical, this is probably the most convenient method for the preparation for the 3-methyl derivative. 3-Methylallantoin is not reduced so readily as allantoin, and after treatment with 1% sodium amalgam in slightly acid solution, yields carbamide, 3-methylhydantoin, and unaltered substance.

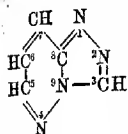
The behaviour of allantoin towards sodium hypochlorite, namely, the elimination of two of the four atoms of nitrogen, is in harmony with

Krimaux's formula,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH} \begin{matrix} \text{NH}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{matrix}$ . The alternative formula, hydroxyacetylenediureine,  $\text{CO} \begin{matrix} \text{NH}\cdot\text{CH}\text{---}\text{NH} \\ \text{NH}\cdot\text{C}(\text{OH})\cdot\text{NH} \end{matrix} \text{CO}$ , cannot

be correct, as such a compound should be stable towards hypochlorite; further, allantoin gives none of the reactions characteristic of hydroxy-compounds.

J. J. S.

**Heterohydroxylic Acids.** CARL BÜLOW and CARL HAAS (*Ber.*, 1910, i, 43, 1975—1984. Compare Abstr., 1909, i, 613—616; this vol., i, 80—81).—As heterohydroxylic acids are denoted the compounds formed by the condensation of 1-amino-1:3:4-triazole with the esters

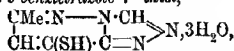


of  $\gamma$ -carboxylic acids. The hydroxylic group in position 7 (annexed formula of 1:2:4:9-benzotetrazole) imparts pronounced acid properties to the compounds, so that they can be titrated readily with standard sodium hydroxide. A comparison of these hydroxylic acid compounds with ordinary carboxylic acid has been made. Their esters cannot be prepared by the ordinary catalytic method of esterification, by

the action of alcohol on the corresponding chloride, or by the action of methyl sulphate on the alkali salts, but are formed when the silver salts are treated with alkyl iodides. They can be benzoylated by the Schotten-Baumann process, but the resulting benzoates are hydrolysed readily by dilute alkalis. A mixture of phosphorus pentachloride and oxychloride transforms the hydroxy-compounds into the corresponding chlorides, which are much more stable than ordinary acyl chlorides; they can be crystallised from alcohol or water, but react readily with potassium hydrogen sulphide, yielding thiols, which are readily oxidisable compounds with pronounced acidic properties. The chlorides form salts with strong acids, but these are fairly readily hydrolysed. The hetero-condensed, heterocyclic system is stable towards concentrated hydrochloric acid, and the acids may be heated with the hydrochloric acid at  $140^\circ$  without appreciable decomposition, but they are readily decomposed when fused with potash at  $280^\circ$ , one of the products being hydrogen cyanide.

7-Hydroxy-5-methyl-1:2:4:9-benzotetrazole (compare Abstr., 1909, i, 615) is best prepared by heating 1-amino-1:3:4-triazole (11 grams) with ethyl acetoacetate (19 grams), first at  $130^\circ$ , then for one hour at  $150^\circ$ , and finally at  $160$ – $170^\circ$  for a quarter to half an hour. The sodium salt,  $C_8H_9ON_4Na$ , crystallises from alcohol in colourless needles; the ethyl ester,  $C_8H_{10}ON_4$ , crystallises from a mixture of benzene and light petroleum, and has m. p.  $170$ – $171^\circ$ ; the benzoate,  $C_{13}H_{10}O_2N_4$ , crystallises from methyl alcohol in long prisms containing methyl alcohol, or from ethyl acetate in cubes, m. p.  $157$ – $158^\circ$ . 7-Chloro-5-methyl-1:2:4:9-benzotetrazole,  $C_8H_9N_4Cl$ , crystallises in long, yellow, glistening needles, m. p.  $185^\circ$ ; the corresponding iodide,  $C_8H_9N_4I$ , crystallises in large, colourless needles, m. p.  $211$ – $212^\circ$ , and forms a hydriodide, m. p.  $196$ – $197^\circ$ , which is obtained when the hydroxy-compound is boiled for six hours with concentrated hydriodic acid and red phosphorus.

5-Methyl-1:2:4:9-benzotetrazole-7-thiol,



crystallises in long, yellow needles, sinters at  $150^\circ$ , but is not com-



plately molten at 280°; its aqueous solution when boiled in contact with the air yields a brown, amorphous, flocculent mass.

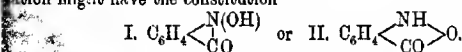
When the chloride is reduced with zinc dust and water, 5-methyl-

2:4:9-benzotetrazole,  $\text{CMe:N}\cdot\text{N}\cdot\text{CH}=\text{N}$ , is formed, and can be

isolated as the *picrate*,  $\text{C}_6\text{H}_5\text{N}_4\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , which crystallises in yellow cubes, m. p. 162—163°. The base crystallises in colourless needles, m. p. 158—159°.

When the hydroxy-compound is heated with five times its weight of phenylhydrazine, it yields 4-anilinoazo-1-phenyl-3-methyl-5-pyrazolone (this vol., i, 233) together with other products. The hydroxy-compound reacts with hydrazine, yielding a salt,  $\text{C}_6\text{H}_5\text{ON}\cdot\text{N}_2\text{H}_4$ , which crystallises from alcohol in large, glistening plates. J. J. S.

**Reduction of Nitro-compounds with Zinc Dust and Acetic Acid.** III. GUSTAV HELLER (*Ber.*, 1910, 43, 1907—1922. Compare *Abstr.*, 1908, i, 867, 913).—[With EDMUND WEIDNER].—The reduction of *o*-nitrobenzamide by zinc dust and 50% acetic acid leads to the formation of small quantities of *o*-azoxybenzamide, m. p. 242° (decomp.), and *o*-azobenzamide, m. p. 284—294° (decomp.), the chief product, however, being benzisooxazolone, which from this method of formation might have the constitution



The first formula harmonises with the amphoteric character of the substance and with the formation of acetyl, benzoyl, and methyl derivatives, but since Reissert's 1-acetoxyoxindole (*Abstr.*, 1909, i, 51), an undoubted *N*-hydroxy-derivative, is reduced to oxindole by zinc dust and 50% acetic acid, whilst 2-acetylbenzisooxazolone is reduced to acetylanthranilic acid, there is no alternative but to accept formula II for benzisooxazolone, a conclusion to which Bamberger and Pyman have arrived at on other grounds (*Abstr.*, 1909, i, 573). *o*-Azobenzamide, when treated with cold concentrated sulphuric acid and sodium nitrite and subsequently heated, yields *benzamide-o*-azobenzoic acid,

$\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 215° (decomp.), and is reduced by glacial acetic acid and zinc dust to *o*-hydrazobenzamide,  $\text{N}_2\text{H}_4(\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}_2)_2$ , m. p. 233°.

The reduction of ethyl *o*-nitrobenzoate by acetic acid and zinc dust yields only ethyl *o*-azoxybenzoate. The reduction of *o*-nitrobenzyl alcohol by zinc dust and 50% acetic acid at 0° and subsequently at 40° yields *o*-azoxybenzyl alcohol and *o*-azobenzyl alcohol.

[With WALTER TISCHNER].—*o*-Nitrophenyl-lactaldehyde is reduced to quinoline by zinc dust, glacial acetic acid, and its own weight of water. *o*-Nitrobenzaldehydediethylacetal is reduced to anthranil, and  $\beta$ -*o*-nitrophenyl- $\alpha$ -methyl-lactaldehyde, prepared from *o*-nitrobenzaldehyde and propaldol, is reduced in a similar manner to 2-methylquinoline, the *hydrochloride*,  $\text{C}_9\text{H}_9\text{Me}\cdot\text{HCl}$ , of which has m. p. 228—230°, and the *base*,  $\text{C}_9\text{H}_9\text{Me}$ , m. p. 164—165°.

*o*-Nitrobenzamide,  $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 164—165°. The reduction of *o*-nitrocinnamic acid by zinc dust and acetic acid in the presence of sodium acetate and water at 40—45° yields about 10%

of *o*-azoxycinnamic acid, m. p. 218° (decomp.), and 50% of *o*-aminocinnamic acid. An aqueous solution of the hydrochloride of the latter and acetic anhydride yields *o*-acetylaminocinnamic acid, m. p. 248—249° (decomp.), which forms carbostyryl when heated, and by warming for one hour with acetic anhydride produces *bis*-*o*:*o* diacetylaminocinnamic anhydride,  $(\text{N}(\text{Ac})_2\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO})_2\text{O}$ , m. p. 156—157°.

*o*-Diacetylaminocinnamic acid, obtained by heating the anhydride with aqueous sodium acetate and a little acetic acid, has m. p. 158°.

Dibromo-*o*-nitrophenylpropionic acid is readily reduced by zinc dust, glacial acetic acid, and its own weight of water at 0°, yielding *o*-aminocinnamic acid and a little *o*-azoxycinnamic acid. C. S.

**Bisazo- and Trisazo-derivatives of Resorcinol.** WILLIAM R. ORNDORFF and B. J. RAY (*Amer. Chem. J.*, 1910, 44, 1—41).—2:4:6-Trisbenzeneazoresorcinol, m. p. 254°, obtained from diazotised aniline hydrochloride (3 mols.) and resorcinol in sodium hydroxide solution, and also from 4:6-bisbenzeneazoresorcinol or from 2:4-bisbenzeneazoresorcinol and benzenediazonium chloride (1 mol.) in sodium hydroxide solution, crystallises in yellowish-brown, pleochroic needles, and when boiled with acetic anhydride and sodium acetate forms a diacetyl derivative, which separates from its solutions in yellow needles, m. p. 201°, by rapid cooling, or in red, pyramidal crystals, m. p. 203°, by slow cooling, and is reconverted into trisbenzeneazoresorcinol by powdered potassium hydroxide suspended in ether.

Wallach and Fischer's  $\beta$ -bisbenzeneazoresorcinol is shown to be 2:4:6-trisbenzeneazoresorcinol contaminated with 4:6-bisbenzeneazoresorcinol, and, similarly, their  $\beta$ -bis-*p*-tolueneazoresorcinol to be a mixture of 2:4:6-tris-*p*-tolueneazoresorcinol (the diacetyl derivative crystallises in yellow needles, m. p. 218°, or in red crystals, mutually interconvertible) and 4:6-bis-*p*-tolueneazoresorcinol (diacetyl derivative, m. p. 198.5°). 2:4-Bis-*p*-tolueneazoresorcinol, m. p. 230.5°, prepared from diazo-*p*-toluene chloride (2 mols.) and resorcinol in sodium acetate solution, forms a diacetyl derivative, m. p. 150°.

2:4:6-Tris-*o*-tolueneazoresorcinol, m. p. 226°, forms a diacetyl derivative, m. p. 176°. 4:6-Bis-*o*-tolueneazoresorcinol has m. p. 197° (Wallach gives m. p. 194—195°), and forms a diacetyl derivative, m. p. 178°. 2:4-Bis-*o*-tolueneazoresorcinol, m. p. 212°, prepared like the para-isomeride, forms a diacetyl derivative, m. p. 130°.

2:4:6-Tris-*n*-naphthaleneazoresorcinol, m. p. 253° (diacetyl derivative, yellow prisms, m. p. 228°, or red, tabular crystals, mutually interconvertible), 2:4-bis-*n*-naphthaleneazoresorcinol, m. p. 243° (diacetyl derivative, m. p. 142°), and bisbenzenazo-*p*-diazoaminobenzene,  $\text{N}(\text{N}_2\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph})_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Ph}$ , m. p. 184°, are also described; the last-mentioned substance is obtained by adding cold alcoholic aminoazobenzene (3 mols.) and acetic acid (9 mols.) to cold sodium nitrite (2 mols.). C. S.

**Heat Coagulation of Proteins.** HARRIETTE CHICK and CHARLES J. MARTIN (*J. Physiol.*, 1910, 40, 404—430).—Crystallised egg-albumin and hæmoglobin were used in the experiments. They are not coagulated by dry heat up to 130°. Heat coagulation is therefore not purely a tem-

perature effect, but a reaction between water and protein. The rate of coagulation of hæmoglobin solutions is proportional to the concentration of the residual hæmoglobin; in the case of egg-albumin, the rate decreases more rapidly than can be accounted for in this way; the crystals are doubtless not homogeneous, and changing conditions are also introduced by the adsorption of acid by the coagulum. Egg-albumin crystals are, as Osborne stated, salts of protein with the acids used in their preparation. Details are given confirmatory of Halliburton's statements as to the effect of acid in hastening the rate of coagulation; it is very considerable. Coagulation of proteins is influenced by temperature in accordance with the law of Arrhenius, but the temperature coefficient is very high, namely, 1.91 per degree for egg-albumin and 1.3 for hæmoglobin.

It is not correct to speak of proteins having any particular coagulation-temperature. Heat coagulation is a reaction between protein and water, and the effect of temperature is merely to accelerate it. Given constant conditions, however, the method may still be used to differentiate proteins, and even to separate them if two proteins are possessed of different reaction rates. The optimum temperature for enzyme actions is also interpreted in a simple way: two operations are at work, that produced by the enzyme, and the destruction of the enzyme by water. If the influence of the temperature on the latter process is greater than on the former, the effect of the enzyme action is counteracted as the temperature rises, and a point is finally reached when the rate of destruction is so great that the enzyme action is arrested.

W. D. H.

**Analysis of Proteins.** ALEXANDRÉ ETARD and ANTOINY VIL (Compt. rend., 1910, 150, 1709—1711. Compare Abstr., 1908, 1, 584; 1909, i, 124).—After removing diamino-acids from the products of hydrolysis of proteins by the method already described, another group of amino-acids may be precipitated by means of ferrocyanic acid.

W. O. W.

**Analysis of Edestin and Zein.** THOMAS B. OSBORNE and L. M. LIDDLE. Sources of Loss in Analysing the Products of Protein Hydrolysis. THOMAS B. OSBORNE and D. BRESEE JONES (*Amer. J. Physiol.*, 1910, 26, 295—304, 305—328).—A number of incomplete analyses of the two proteins mentioned are described in the first paper. The second paper, as its title indicates, should be studied in detail by those interested in protein analysis. The following table of cleavage products of zein is considered nearer the truth than any previously published.

Glycine.....	0.00	Tyrosine.....	55
Alanine.....	9.79	Arginine.....	1.55
Valine.....	1.88	Histidine.....	0.88
Leucine.....	19.55	Lysine.....	0.09
Proline.....	9.04	Tryptophan.....	0.40
Phenylalanine.....	6.55	Ammonia.....	5.81
Aspartic acid.....	1.71	Carbohydrate.....	0.00
Glutamic acid.....	26.17		
Serine.....	1.02	Total.....	85.25

W. D. H.

**Fibrin-ferment.** C. GESSARD (*Compt. rend.*, 1910, 150, 1617—1618. Compare Abstr., 1909, ii, 682).—Whilst hæmoglobin is freed from mæmase by a single crystallisation, the operation must be repeated several times to remove the fibrin-ferment. The latter is carried down by calcium phosphate when this is precipitated from a solution of fibrin (obtained by whipping) in physiological salt solution. After washing the calcium phosphate, the fibrin-ferment may be extracted by maceration with horse serum, previously heated for an hour at 60°.

W. O. W.

**Behaviour of Hæmoglobin towards Hydrazine and the Question of the Capacity of the Colouring Matter of Blood for Combining with Gases.** E. LERSCHE (*Zeitsch. physiol. Chem.*, 1910, 67, 177—191).—The experiments of Hüfner have been repeated and extended (Abstr., 1889, 426; 1900, i, 267; *Arch. Anat. and Physiol.*, 1894, 156). The spectrophotometric method has been used, and the values of  $c/\epsilon$  for hæmoglobin with and without the addition of hydrazine hydrate determined under different conditions. The results show that it is the hydrazine and not some impurity which reacts with the hæmoglobin. The effect of the addition of hydrazine hydrate can also be detected by the naked eye. Methæmoglobin is also affected by hydrazine. Both changes consist partially of reductions, but other reactions take place at the same time.

Hæmoglobin and hæmin solutions behave quite differently towards hydrazine, and the reactions are being subjected to further examination.

The effect of the presence of hydrazine on the solubility of carbonic oxide in hæmoglobin has been studied. Also, the effects of concentration of the hæmoglobin solution and of pressure have been examined (compare Manchot, this vol., ii, 137). Some of the differences found can be explained on the view that the solution of the gas is partly physical, and thus the solubility falls under Henry's Law, but chemical combination also occurs.

J. J. S.

**Colouring Matter of Blood.** LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1910, 67, 195—196).—Polemical in reply to Küster (this vol., i, 529).

J. J. S.

**Oxidation of Pure Oxyhæmoglobin by Hydrogen Peroxide.** L. SZRETER (*Compt. rend.*, 1910, 151, 97—99. Compare Abstr., 1909, i, 620).—Hydrogen peroxide acts on oxyhæmoglobin at 37°, bringing about simple addition of oxygen, and converting it into a substance which, after purification by dialysis, was obtained in colourless, brilliant spangles containing 0.98% of iron in organic combination. Before dialysis, the substance was hygroscopic and much less stable.

W. O. W.

**Behaviour of *d*-Leucyl-*l*-tryptophan towards Autolytic Ferments.** HANS FISCHER (*Ber.*, 1910, 43, 1963—1964).—The author confirms his previous statement that *d*-leucyl-*l*-tryptophan is attacked by autolytic ferments, including yeast extract. Abderhalden and Schuler's seemingly negative results (this vol.,

1, 304) are attributable to the fact that the products of hydrolysis have much the same rotation as the original peptide. J. J. S.

**Chondroitinsulphuric Acid.** KURA KONDO (*Biochem. Zeitsch.*, 1910, 28, 116—130).—The acid was prepared from the cartilage of the nasal septum of pigs, which was treated first with 2% potassium hydroxide for two days. The alkaline liquid, after filtration, was just acidified with acetic acid, and boiled with barium carbonate; this treatment was continued until the whole of the protein was coagulated, and the liquid, after filtration and concentration, was thrown into three times the volume of glacial acetic acid; after evolution of the precipitate thus formed in water and reprecipitation with glacial acetic acid, the free acid thus obtained was neutralised with sodium or potassium hydroxide, the solution concentrated, and the sodium or potassium salt precipitated by the addition of alcohol. The composition of the acid prepared thus corresponded approximately with the formula  $C_{15}H_{27}O_{16}NS$ . It gave strongly the orcin and phloroglucinol reactions, and yielded fufuraldehyde after treatment with acids. It gave also, but in very small yield, an osazone-like substance, melting at  $143^{\circ}$ . The salts are levorotatory. The benzoyl derivatives of the scission products obtained by treatment of the chondroitinsulphuric acid with 2—3% hydrochloric acid were also investigated. The product obtained did not contain more than five benzoyl groups. S. B. S.

**Lipids. X. The Detection of Galactose in Lipids.** SIGMUND FRÄNKEL and KURT LINNERT (*Biochem. Zeitsch.*, 1910, 28, 41—43).—The authors isolated the galactose obtained by the hydrolysis of brain lipids in the form of the  $\alpha$ -phenylmethylhydrazone, which melted at  $189^{\circ}$ . They also isolated the sugar by hydrolysing with sulphuric acid, separating the acid after hydrolysis by barium hydroxide and carbonate, evaporating the filtrate, dissolving the residue from evaporation in methyl alcohol, and then adding ether. After several days, the sugar could be separated in crystalline form. S. B. S.

**Lipids. XII. The Phosphatides of Horse Pancreas.** SIGMUND FRÄNKEL and THEODOR R. OFFER (*Biochem. Zeitsch.*, 1910, 28, 53—54).—From hot acetone extract of horse pancreas a crystalline substance separates on cooling, which, after filtering from liquid fats, washing with 90% alcohol, and recrystallising from hot absolute alcohol, melts at  $120^{\circ}$ . Two grams were obtained from 4½ kilos. of the fresh organ. The analyses corresponded with the formula  $C_{72}H_{147}O_{11}N_2P$ ; the substance is a saturated diaminomono-phosphatide. S. B. S.

**The Protective Action of Proteins on Enzymes.** LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1910, 28, 9—13).—The addition of proteine (egg-white) protects enzymes from the deleterious action of acids and bases. This protective action could be demonstrated in the cases of  $\delta$ -emulsin, diastase and invertin. S. B. S.

**The Inactivation of Ferments, and the Formation of Antiferments in Presence of Collodium and Other Membranes.** ALBERT E. PORTEE (*Biochem. Zeitsch.*, 1910, 25, 301—304).—The

investigations included the study of pepsin, trypsin, rennet, steapsin, ptyalin, emulsin, and taka-diasatase. All these ferments, with the exception of taka-diasatase, lose their activity in presence of collodion membranes, and acquire, with the exception of ptyalin, an antifermmentative action. Colloids other than collodion, such as egg-white membranes and gelatin, exert a similar action. S. B. S.

**Inversion of Sucrose by Invertase. IV. Influence of Acids and Alkalis on the Activity of Invertase.** C. S. HUDSON and H. S. PAINE (*J. Amer. Chem. Soc.*, 1910, 32, 774—779; *Zeitsch. Ver. deut. Zuckerind.*, 1910, 634—641. Compare Abstr., 1908, i, 605, 856; 1909, i, 554).—The work described in this paper was undertaken with the object of determining the conditions of acidity and alkalinity which render invertase inactive, and also those which cause its total destruction.

It has been found that acids and alkalis in small concentrations influence the activity of invertase, whilst in large concentrations they cause its destruction. The destruction by acid at 30° proceeds at a scarcely appreciable rate at a concentration of 0.01*N*, and increases rapidly with the acidity until it becomes almost instantaneous at 0.05*N*. The rate of destruction follows the formula for unimolecular reactions. The destruction by alkali at 30° commences at a point a little below 0.01*N*, and is almost instantaneous at 0.045*N*. The rates of destruction are plotted as curves.

The activity of invertase in acid solutions which are not strong enough to destroy the enzyme have been determined for hydrochloric, hydrobromic, nitric, phosphoric, sulphuric, boric, oxalic, tartaric, citric, and acetic acids. The activity has been found to depend almost entirely on the concentration of hydrogen ions in the solution. The activity of invertase is zero in alkaline solutions, rises to a maximum in very weakly acid solutions, and decreases with increasing acidity. E. G.

**Invertase.** NIRO MASUDA (*Zeitsch. physiol. Chem.*, 1910, 66, 145—151. Compare Salkowski, Abstr., 1909, i, 752).—The addition of yeast gum to an invertase solution which is free, or nearly free, from gum increases the activity of the enzyme to a slight, although perceptible, extent. Invertase solutions (that is, filtered yeast extract) lose almost 70% of their activity on keeping for twenty-four hours, but the activity then diminishes only very slowly. Old preparations full of moulds and bacteria retain their inverting power. Invertase produces slightly more invert sugar in 10% than in 5% sucrose solution. Increase of the amount of ferment does not produce a proportional increase in the amount of invert sugar formed. E. F. A.

**Destruction of Invertase by Acids and Alkalis.** H. S. PAINE (*Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, 7, xli—xlii).—Invertase was placed at 30° in various concentrations of hydrochloric acid and sodium hydroxide for different times. All samples were then brought to the optimum acidity in sucrose solutions of the same strength and volume. Action was allowed to take place

for an hour, and the velocity-coefficient calculated from the formula for unimolecular reactions; from this the coefficient of the rate of destruction was derived.

Destruction commenced at about 0.015*N*-acid and 0.01*N*-alkali solution, requiring five to six hours for completion. In 0.05*N*-acid and 0.04*N*-alkali destruction occurred in five minutes.

W. D. H.

**Studies on Enzyme Action. XIII. Enzymes of the Emulsin Type.** HENRY E. ARMSTRONG and EDWARD HORTON (*Proc. Roy. Soc.*, 1910, *B*, 82, 349—367. Compare Abstr., 1908, i, 745).—Contrary to the statement of Dunstan, Henry, and Auld (Abstr., 1907, ii, 572), it is shown that phaseolunatin, the glucoside present in *Phaseolus lunatus* seeds, in flax seed, and in cassava is invariably hydrolysed by almond-emulsin, although only to a very small extent. Moreover, amygdalin is found to be as little attacked by the *Phaseolus* enzyme (phaseolunatase) as is phaseolunatin by emulsin, when the comparison is made under molecularly similar conditions.

The observation made by Dunstan, Henry, and Auld (*loc. cit.*), that methyl- $\alpha$ -glucoside is hydrolysed by phaseolunatase, is not confirmed. Similarly, the enzyme was found to be inactive towards maltose. Methyl- $\beta$ -glucoside, however, is attacked by phaseolunatase, although much less readily than by emulsin, an observation which has not hitherto been recorded.

The authors confirm the statement of Dunstan and his co-workers, that phaseolunatin is hydrolysed by an extract of dried yeast, but attribute this to the action, not of maltase, but of the "emulsin" discovered in yeast by Henry and Auld (Abstr., 1906, ii, 114).

The conclusion arrived at by Dunstan, Henry, and Auld, that phaseolunatin is an  $\alpha$ -glucoside, is controverted by the authors. Experiments are described which tend to indicate that the glucose is liberated from phaseolunatin in the  $\beta$ -form, but the question is complicated by the fact that the enzyme itself suffers a change in optical rotatory power when treated with the small quantity of alkali necessary to effect the mutarotation of the liberated glucose. Since all efforts to discover in *Phaseolus* seeds an enzyme capable of effecting the hydrolysis of  $\alpha$ -glucosides failed, the conclusion is drawn that phaseolunatin is a  $\beta$ -glucoside, and that the correlated enzyme phaseolunatase is of the  $\beta$ -type.

Although only very slightly active towards amygdalin, phaseolunatase is almost as active as almond-emulsin towards *L*-mandelonitrile glucoside. This may be partly accounted for by the absence from phaseolunatase of amygdalase, but no explanation is offered of the fact that, whilst phaseolunatase attacks both phaseolunatin and *L*-mandelonitrile glucoside equally, almond-emulsin acts only very slightly on the former glucoside.

Pressed yeast juice and the enzyme extracted from *Anthyllus vulgaris* seed are similarly more active towards *L*-mandelonitrile glucoside than towards amygdalin, and only act very slightly on phaseolunatin. The differences in the activity of vegetable cytase towards the three cyanophoric glucosides are less marked, although in the same direction.

It is pointed out that the experiments assumed by Auld (*Trans.*, 1908, 93, 1277), to prove that the glucose liberated from amygdalin by yeast extract is in the  $\alpha$ -form, whilst that set free when *l*-mandelonitrile glucoside is hydrolysed is in the  $\beta$ -form, are invalidated by the fact that both glucosides are racemised fairly rapidly by alkali, with consequent change in their optical rotatory powers.

A comparison is given of the results obtained when estimating hydrogen cyanide by the method devised by the authors, and by the modification of Fordos and Gelis' method employed by Dunstan and his colleagues. From this it seems that the latter method is only to be preferred in the estimation of quite minute amounts of hydrogen cyanide.

The authors advocate the employment, in experiments with hydrolytic enzymes, of solutions (of the various hydrolytes) of the same molecular concentration, in order that the concordance between the results obtained by different workers (when this exists) may be rendered apparent.

E. H.

**The Separation of the Racemic Cyanohydrins by Emulsin.** LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1910, 26, 7—8. Compare *Abst.*, 1909, i, 74).—*l*-Benzaldehydecyanohydrin can be obtained from the racemic variety by the action of  $\delta$ -emulsin when air is led through the mixture. "This has the effect of removing one of the products of hydrolysis, namely, the hydrogen cyanide."

S. B. S.

**Asymmetric Syntheses by means of Enzymes. III.** LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1910, 26, 1—6).—In addition to the method already described, namely, by heating for a long time at 40—50° for separating the  $\delta$  (hydrolysing) emulsin from the  $\sigma$  (synthesising) enzyme, the author finds that a separation can also be accomplished by treating the mixtures of enzymes for a short time with acids and then neutralising with alkali. The quantity of acid and time of action must be determined for every sample of emulsin investigated, and great variations are found in the different preparations. The author also describes various other methods attempted for separating the enzymes, which did not lead to the desired effect.

S. B. S.

**Biology of Enzymes. Action of Heat on the Lipases and Amylases of Pancreatic Juice.** SANATO VISCO (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 597—603).—The lipolytic power of pancreatic juice was determined by adding to it sweet almond oil and titrating with alcoholic sodium hydroxide the oleic acid formed after the mixture had been a certain time in a thermostat. The amylolytic power was measured by estimating the sugar formed from starch in similar circumstances. It was found that the lipase slowly changes at the ordinary temperature, and loses its activity completely in a few hours at 39—41°. The ferment is not affected by the higher temperature, however, if it has already commenced to act on the oil. The amylase, when kept at 39—41°, at first shows slightly increased activity, but the latter diminishes, although slowly, on prolonged exposure to that temperature.

R. V. S.



**Plant Peroxydases. I. New Method of Preparing Peroxydases.** A. W. VAN DER HAAR (*Ber.*, 1910, 43, 1321—1327).—Bach (*Abstr.*, 1908, i, 746; this vol., i, 291) has claimed that both peroxydases and oxydases can be obtained absolutely free from manganese and iron. Peroxydase has now been purified by the author a stage further than by Bach, until all coagulable protein had been removed, but it has not been possible to remove absolutely all manganese. After precipitation of impurities by basic lead acetate, the proteins can be coagulated by heating the solution to 90° without destroying the peroxydase. Throughout the process of purification the oxidising power was contrasted with the amount of manganese present, but no relation between these two factors was evident. E. F. A.

**Plant Peroxydases. II. Hedera-Peroxydase, a Glucoprotein.** A. W. VAN DER HAAR (*Ber.*, 1910, 43, 1327—1329).—A carefully purified peroxydase preparation from the leaves of *Hedera helix* contained 2% of ash, and the solution, which lacked other known enzymes, showed the biuret, xanthoproteic, and Millon's reactions; it contained organically combined nitrogen and sulphur, but was free from phosphorus. When boiled with 3% hydrochloric acid, it acquired the power of reducing Fehling's solution, and formed a phenylosazone, m. p. 165°. In addition, the peroxydase was non-coagulable, and could not be salted out. It is regarded in consequence as a glucoprotein. It contained 0.0007% of manganese, equivalent to 0.03% of the ash. The peroxydase from potatoes also yielded a carbohydrate on treatment with acids. E. F. A.

**Action of Haloid Derivatives of Sulphur on Organomagnesium Compounds.** ENOS FERRARIO (and, in part, H. VIXAR) (*Bull. Soc. chim.*, 1910, [iv], 7, 518—527).—The investigation of the action of sulphur chloride, dichloride, and tetrachloride on aromatic and aliphatic magnesium haloid compounds showed that sulphurisation, chlorination, and condensation proceeded simultaneously; thus with sulphur dichloride the following reactions probably occurred:  $2\text{PhMgBr} + \text{SCl}_2 = \text{SPh}_2 + 2\text{MgBrCl}$ ;  $2\text{PhMgBr} + 2\text{SCl}_2 = 2\text{PhCl} + 2\text{MgBrCl} + \text{S}_2$ ;  $4\text{PhMgBr} + 2\text{SCl}_2 = 2\text{Ph}-\text{Ph} + 4\text{MgBrCl} + \text{S}_2$ ;  $2\text{PhS-MgBr} + \text{SCl}_2 = \text{S}_2\text{Ph}_2 + 2\text{MgBrCl}$ . The products of the reaction were separated by fractional distillation under diminished pressure.

The mixture, obtained by the action of sulphur chloride on magnesium phenyl bromide and the addition of water, contained chlorobenzene, bromobenzene, phenyl sulphide, diphenyl and pheoyl disulphide, trisulphide, and tetrasulphide. Sulphur dichloride with the same compound furnished the same products as did also sulphur tetrachloride, except that in the latter case more chlorobenzene was formed. In this reaction the tetrachloride behaved as a mixture of sulphur dichloride and chlorine.

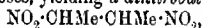
Sulphur chloride reacted with magnesium methyl iodide to give methyl chloride and methyl sulphide, disulphide, and trisulphide. The action with magnesium ethyl bromide was analogous, ethyl chloride, sulphide, and disulphide being formed. T. A. H.

## Organic Chemistry.

Critical Constants of Acetylene and Cyanogen. ERRÔRE CARDOSO and GEORGES BAUME (*Compt. rend.*, 1910, 151, 141—143).—The following values have been obtained for the critical constants of pure acetylene and cyanogen. Acetylene has a critical temperature  $35.5^{\circ}$ , and critical pressure 61.5 atmospheres (compare Mathias, *Abstr.*, 1909, ii, 552). Cyanogen has a critical temperature  $128.3^{\circ}$ ; pressure, 59.6 atmospheres. The author considers that the cyanogen employed in Dewar's determinations was not free from air, and that consequently the results obtained were too low (*Abstr.*, 1885, 331).  
W. O. W.

The Decomposition of Certain Salts of Silver. ANGELO ANGELI and L. ALESSANDRI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 734—733. Compare *Abstr.*, 1909, i, 739).—The dinitro-derivatives of stilbene have been stated to be converted into resins by the action of alkali, whilst the compounds obtained by the authors from the silver salt of  $\alpha$ -isobutyltoluene yield definite compounds. It is now shown that the action of sodium ethoxide on  $\alpha$ -dinitrostilbene yields the compound  $\text{OEt}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{NO}_2$ , identical with that obtained by the authors, and yielding the compound  $\text{CHPh}\cdot\text{CPh}\cdot\text{NO}_2$  when acted on with piperidine.

Other nitro-derivatives react in a similar manner. The silver salt of nitroethane decomposes, yielding a dinitrobutane,



which melts at  $41^{\circ}$  and decomposes at  $150^{\circ}$ , but may be distilled under reduced pressure. At the same time a small quantity of the compound  $\text{CHMe}\cdot\text{CMe}\cdot\text{NO}_2$  appears to be formed.

The pure dinitro-compound is decomposed by potassium methoxide, but the original oil yields large, bright yellow crystals of a salt,  $\text{C}_8\text{H}_8\text{O}_2\text{N}_4\text{K}_2$ , apparently a condensation product.

It was not found possible to reduce the dinitrobutane directly to diacetyldioxime, a hydroxylamine derivative being formed, which is not readily oxidised to the dioxime. The reduction may, however, be effected by means of zinc dust and acetic acid in alcohol, concentrating the filtrate, and adding hydrochloric acid, followed by the addition of an excess of ammonium chloride, ammonia, and nickel sulphate, afterwards passing a current of air. A heavy, pink precipitate of the nickel compound of diacetyldioxime is obtained (Tschugaeff, *Abstr.*, 1905, ii, 613), and yields the dioxime when decomposed with acid.

The silver salt of nitropentane yields colourless prisms of dinitrodecane,  $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_2$ , m. p.  $109$ — $110^{\circ}$ .

Piperonaldoxime, nitrocinnamene, and phenyldiazonitroethane also yield unstable salts, but definite compounds have not been isolated from their products of decomposition.

C. H. D.

**Action of Metallic Oxides on the Primary Alcohols.** PAUL SABATIER and ALPHONSE MAILHE (*Ann. Chim. Phys.*, 1910, [viii], 20, 289—352).—Mainly a résumé of work published by the present authors and others (compare Jahn, Abstr., 1880, 794; Grigorieff, *J. Russ. Phys. Chem. Soc.*, 1901, 33, 173; *Bull. Soc. chim.*, 1902, [iii], 26, 612; Ipatieff, Abstr., 1901, i, 248; 1902, i, 335; 1903, i, 593; Sabatier and Mailhe, Abstr., 1908, i, 594, 713; 1909, i, 546; this vol., i, 294; Senderens, Abstr., 1908, ii, 166; 1909, i, 127, 286; Sabatier and Senderens, 1905, i, 333, 401). Contrary to the statement made previously (Abstr., 1909, i, 546), methyl alcohol when decomposed by titanium oxide gives formaldehyde.

A table is given showing the composition of the gas evolved, and its rate of evolution, when a fixed quantity of ethyl alcohol is decomposed by the various oxides examined.

An explanation similar to that proposed for the decompositions effected by finely-divided metals is suggested for the catalyses produced by the oxides.

E. H.

**Preparation of Pyruvic Acid.** ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, 43, 2188—2189).—A 60% yield of pure pyruvic acid, b. p. 59—60°/12 mm., can be obtained by distilling a mixture of 500 grams of tartaric acid and 780 grams of commercial potassium hydrogen sulphate from a copper retort of about 2 litres capacity. The process requires about thirty minutes, and no frothing occurs. As the metal is corroded by the sulphate, it is advisable to cover the interior of the retort with asbestos paper and water glass. The receiver is well cooled, and is provided with an upright condenser, the upper end of which is closed with a plug of cotton wool. The crude distillate is purified by fractional distillation under reduced pressure.

J. J. S.

**Degradation of Cholic Acid. II. The Distillation Products of Cholic and Bilianic Acids.** OTTO VON FÜRTH and EMIL LENK (*Biochem. Zeitsch.*, 1910, 26, 406—434).—Two main products were obtained by the distillation both of cholic and bilianic acid, the one of oily and the other of wax-like nature. The oily product is a hydrocarbon with something between 12 and 17 carbon atoms (as it gave varying numbers for the molecular weight determined by the ebullioscopic method in various solvents). It readily resinifies. The wax-like substance contains oxygen. The authors give an account of the action of halogens of permanganate and of nitric acid on the oily substance. No products have yet been isolated in a pure state.

S. B. S.

**Preparation of Cystine.** OTTO FOLIN (*J. Biol. Chem.*, 1910, 8, 9—16).—Cystine is easily prepared from wool by the following method, which differs mainly from Mönner's in the use of strong acid; 200 c.c. of strong hydrochloric acid to each 100 grams of wool are boiled in a flask (with a condenser consisting of a tube 2 or 3 feet long) until the biuret test is negative, usually three to five hours. Solid sodium acetate is added until the Congo-red reaction for mineral acid

is negative; a dark heavy precipitate, which contains practically all the cystine is obtained; this is filtered and washed with cold water. The filtrate on keeping deposits a second precipitate, consisting mainly of tyrosine. The crude cystine is dissolved in 3 to 5% hydrochloric acid and decolorised with bone-black, which has been previously digested with dilute hydrochloric acid to remove the calcium phosphate. The filtrate is heated to boiling, and the cystine precipitated by the slow addition of hot concentrated sodium acetate solution.

W. D. H.

**Action of Ozone on Organic Compounds. II. CARL D. HARRIES** (*Annalen*, 1910, 374, 288-368. Compare Abstr., 1906, i, 225).—The paper contains a discussion of work published during the last five years on the mode of attack of ozone on various classes of organic compounds, the behaviour of ozone derivatives during fission by water or other reagents, the constitution of the ozonides, the special behaviour towards ozone of substances containing different kinds of double linkings, the behaviour of the solvent during ozonisation, a description of the ozonising apparatus, and the effect of varying concentration of ozone.

The following new work is described. Ethyl alcohol has been ozonised in the hope of showing that the first step in the oxidation is the formation of Baeyer and Villiger's ethyl hydroperoxide,  $\text{EtO}\cdot\text{OH}$ . The substance obtained, however, is not identical with, but must be nearly allied to, ethyl hydroperoxide; possibly it is the tautomeric peroxide,  $\text{Et} \begin{smallmatrix} \diagup \\ \text{O} \end{smallmatrix} \text{O} \cdot \text{O}$ . It has h. p. 55-56°/10 mm.,  $D_{25}^{25}$  1.028,  $n_D^{20}$  1.40924, explodes violently when heated, contains 11.3% of active oxygen, reduces Fehling's solution and ammoniacal silver nitrate, and yields hydrogen peroxide and acetaldehyde when decomposed by water. The oxidation of  $\beta$ -hydroxypropioacetal by ozone yields  $\beta$ -hydroxypropionaldehyde, not the semi-acetal of malondialdehyde as previously stated (Harries, Abstr., 1904, i, 15).

[By RUDOLF KORTSCHAU.]—Langheld has shown that by direct ozonisation heptaldehyde yields a peroxide,  $\text{C}_7\text{H}_{14}\text{O}_2$ . When treated with 15% ozone in ethyl chloride, or with 7% ozone in methyl chloride, the aldehyde yields a substance,  $D_{25}^{25}$  0.9504,  $n_D^{20}$  1.42867, the composition of which approximates to the formula  $\text{C}_8\text{H}_{16}\text{O}_3$ . Similarly, octaldehyde, when ozonised in ethyl chloride by 15% ozone, yields a peroxide,  $\text{C}_8\text{H}_{16}\text{O}_2$ ,  $D_{25}^{25}$  0.9088,  $n_D^{20}$  1.42767, or by more prolonged action a substance,  $D_{25}^{25}$  0.9497,  $n_D^{20}$  1.43267, approximating to the composition  $\text{C}_8\text{H}_{16}\text{O}_3$ . By direct ozonisation with 7% ozone at 0°, nonaldehyde yields a peroxide,  $\text{C}_9\text{H}_{18}\text{O}_2$ , m. p. 6°, which is not identical with the peroxide, m. p. 73°, obtained by the decomposition of oleic acid ozonide; in methyl chloride the aldehyde is converted by 7% ozone into a substance,  $D_{25}^{25}$  0.9334,  $n_D^{20}$  1.43167, the composition of which approximates to  $\text{C}_9\text{H}_{18}\text{O}_3$ . isoValeraldehyde yields a peroxide,  $\text{C}_9\text{H}_{18}\text{O}_2$ ,  $D_{25}^{25}$  0.9462,  $n_D^{20}$  1.40826, by direct treatment with 15% ozone in a freezing mixture, and a substance,  $\text{C}_9\text{H}_{18}\text{O}_3$  (?),  $n_D^{20}$  1.40335, when ozonised in ethyl chloride. isoButaldehyde and acetaldehyde behave in a similar manner. Formaldehyde in methyl chloride is quantitatively

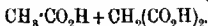
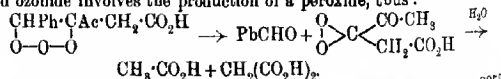
converted into trioxymethylene by treatment with ozone. By treatment with sodium hydroxide, the preceding peroxides are converted into the sodium salts of the corresponding acids. The fatty acids do not yield per-acids by treatment with ozone, but are merely oxidised.

[With H. O. TÜRK.]—To the results obtained by Harries and Türk by the exhaustive ozonisation of mesityl oxide and phorone (Abstr., 1905, i, 413) the following are to be added. By treatment with 12–14% ozone in an atmosphere of dry carbon dioxide, mesityl oxide, cooled by a freezing mixture, yields a normal ozonide,  $C_6H_{10}O_4$ ,  $D_{15}^{20} 1.0754$ ,  $n_D^{20} 1.39409$ , which is decomposed by water, yielding acetone, methylglyoxal, and formic and acetic acids; when carefully heated at  $105^\circ$ , the ozonide yields carbon dioxide, acetone, acetone peroxide, formic and acetic acids, methylglyoxal, and mesityl oxide, which is identified in the form of its *p*-nitrophenylhydrazone.

By ozonisation in carbon tetrachloride, care being taken to avoid an excess of ozone, methylheptenone yields a normal ozonide,  $C_8H_{14}O_4$ , which resembles Langheld's perozone in many respects. It is decomposed by water, yielding acetone peroxide, acetone, lævulinic acid, lævulaldehyde (isolated as phenylmethylidihydropyridazine), and a small amount of a peroxide of the last.

Mesoxaldialdehyde, in the form of its *tri-p*-nitrophenylhydrazone, m. p.  $277^\circ$  (decomp.), has now been definitely detected amongst the products of decomposition of phorone diozonide by water (compare Harries and Türk, *loc. cit.*). When a chloroform solution of phorone is incompletely ozonised, a *monoozonide* seems to be formed, since dimethylacrylic acid occurs amongst its products of decomposition by water. Mesoxaldialdehyde, together with benzaldehyde and benzoic acid, is formed by decomposing with water the viscous, yellow oil formed by ozonising a chloroform solution of dibenzylideneacetone until the greenish-yellow colour has disappeared.

[By KARL KIRCHER.]—It has been stated previously (Harries and Kircher, Abstr., 1907, i, 466) that the ozonide of  $\beta$ -benzylidenelævulinic acid is decomposed by water, yielding benzaldehyde, benzoic acid, and diacetylcarboxylic acid, and also that diacetylcarboxylic acid is a comparatively stable compound. It is now found that malonic acid is also present amongst the products of decomposition of the ozonide, and also that diacetylcarboxylic acid is an unstable substance, being partially decomposed even by the evaporation of its aqueous solution in a vacuum. Since the products of its decomposition are malonic and acetic acids, it seems very probable that the decomposition of  $\beta$ -benzylidenelævulinic acid ozonide involves the production of a peroxide, thus:



Diacetylcarboxylic acid forms a *bis-p*-nitrophenylhydrazone, m. p.  $295^\circ$  (decomp.), crystallising in red prisms, and a *bis-semicarbazone*, m. p.  $240^\circ$  (decomp.).

[By WALTER FRANCK.]—Further information is given respecting the ozonides of oleic acid (compare Harries and Franck, Abstr., 1909, i, 131). The normal ozonide is always produced, independent of the concentration of the ozone, when care is taken, by testing with bromine

in acetic acid, to avoid any excess of the amount of ozone theoretically required; directly this limit is exceeded, the perozonide is formed. The normal ozonide is decomposed by hot glacial acetic acid, yielding nonaldehyde and its peroxide, nonolic acid, azelaic acid, and its peroxide and semialdehyde. Decomposition by glacial acetic and formic acids prevents the formation of peroxides, but otherwise gives the same products. The decomposition of an ethereal solution of the ozonide by moist ethereal sulphur dioxide or by aluminium amalgam also yields the same products. The normal ozonide of oleic acid forms salts, of which the ammonium, sodium, and copper salts are described, when care is taken to exclude moisture and to prevent rise of temperature. Nonaldehyde peroxide, m. p.  $72^{\circ}$ , b. p.  $80-90^{\circ}/13$  mm., is changed to sodium nonoate by sodium hydroxide, and liberates only about 50% of the theoretical quantity of iodine from acidified potassium iodide in consequence of the change of about one-half of the peroxido into the isomeric acid.

When oleic acid is submitted to prolonged treatment with 10% ozone, or when its solution in glacial acetic acid is treated with 16—18% ozone for four hours, a *superperozonide*,  $C_{15}H_{31}O_7$ , is formed, which has  $D_4^{20}$  1.079,  $n_D^{20}$  1.46817, is not particularly explosive, and yields by decomposition with warm water the same products as the other ozonides of oleic acid.

The normal ozonide,  $C_{15}H_{31}O_6$ ,  $D_4^{20}$  1.027,  $n_D^{20}$  1.46171, of elaidic acid\* is prepared in a similar manner to, and does not differ in any respect from, the normal ozonide of oleic acid; it has not yet been settled whether the two are identical. C. S.

**The Scission of Sugars. Synthesis of Sugar from Formaldehyde.** WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1910, 26, 231—237. Compare this vol., i, 95).—Experiments were carried out to determine whether the equilibrium between formaldehyde and the aldehydes with more carbon atoms (hexoses and pentoses) was the same in the building-up process from aldehyde as in the degrading processes from sugars, when the same substances are present at the same time in a mixture. The question could not be definitely answered, owing to the secondary process affecting only the formaldehyde, by means of which it was converted into methyl alcohol and acetaldehyde. On treatment of formaldehyde solutions with lead hydroxide, a pentose seemed to be formed, which could not be isolated in the form of a pure osazone. Saccharic acid could be identified. S. B. S.

**Phosphoric Esters of Some Polyhydric Alcohols and Carbohydrates.** ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 823—827. Compare this vol., i, 157).—It is shown that certain polyhydroxylic compounds combine with phosphoric acid without undergoing any change of structure, a fact of importance in studying naturally occurring compounds.

When 25 grams of mannitol are heated for ten hours with 120 grams of phosphoric acid, D 1.7, to  $120-130^{\circ}$ , the product being decolorised with animal charcoal and purified by means of the barium

salt, a syrupy liquid, having the composition  $C_6H_{20}O_{24}P_6$ , is obtained, and is thus *mannitol hexaphosphate*. Quercitol yields a *pentaphosphate*,  $C_6H_{17}O_{20}P_5$ , whilst dextrose forms a *heptaphosphate*,  $C_6H_{20}O_{28}P_7$ , the aldehyde group behaving as two hydroxyl groups. C. H. D.

**Phosphoric Acid Esters of Carbohydrates. II. Sucrosulphuric Acid and the Phosphoration of Protein.** CARL NEUBERG and HUGO POLLAK (*Ber.*, 1910, 43, 2060—2068; *Biochem. Zeitsch.*, 1910, 26, 514—534. Compare this vol., i, 157).—Dextrose dissolved in water and mixed with finely-divided calcium carbonate is well cooled and continuously shaken from eight to ten hours with phosphoryl chloride dissolved in chloroform. The liquid is then concentrated in a vacuum, and the *calcium salt of dextrose phosphoric acid ester* precipitated by pouring into alcohol. It is a colourless, soluble powder, stable in the atmosphere, and reduces Fehling's solution. It only shows the reactions of phosphoric acid after hydrolysis with boiling mineral acids, and is not fermentable until hydrolysed.

To prepare sucrosulphuric acid, potassium pyrosulphate is slowly added to a mixture of sucrose and potassium hydroxide at 60—70°. After twenty-four hours, inorganic sulphuric acid is removed with barium hydroxide and *barium sucrosulphate*, obtained as a colourless powder which only reduces Fehling's solution after hydrolysis. It has  $[\alpha]_D^{20} + 26.09^\circ$ . The sulphuric acid is very firmly bound in the molecule, but if the equivalent quantity of cold hydrochloric acid is added to the barium salt, the liquid obtained reduces Fehling's solution after a time. The *calcium salt* is similar; it is not fermentable.

The simple amino-acids react with phosphoryl chloride in presence of alkali to form organic phosphoric acid compounds, but these could not be isolated. The proteins behave similarly, but in this case the phosphorus compounds are precipitated by acetic acid. These phospho-proteins are similar to the natural products, and are digested by trypsin and pepsin. E. F. A.

**Stachyose and Lupeose.** ERNST SCHULZE (*Ber.*, 1910, 43, 2230—2234).—Lupeose ( $\beta$ -galactan: Abstr., 1892, 1171) from *Lupinus luteus* and *L. angustifolius* has the same optical rotation and gives the same yield of mucic acid on oxidation as stachyose, whereby saccharic acid is also formed. It is a tetrasaccharide composed of residues of galactose (2), dextrose, and lævulose, but since it cannot be caused to crystallise in the same way as stachyose, the two are not yet regarded as identical. When purified by pouring the aqueous solution into methyl alcohol, and precipitating this solution with absolute ethyl alcohol, it has  $[\alpha]_D + 148^\circ$ . E. F. A.

**Oxidation and Hydrolysis of Glycogen Under the Action of Hydrogen Peroxide.** MME. Z. GATIN-GRUZEWSKA (*Bull. Soc. chim.*, 1910, [iv], 7, 744—747. Compare Würster, Abstr., 1887, 683; Asboth, Abstr., 1893, i, 384; Gatin-Grużewska, Abstr., 1909, i, 209).—If a 1% solution (100 c.c.) of glycogen is mixed with pure hydrogen peroxide (5 c.c.) and kept at 37°, the opalescent liquid

gradually becomes more and more limpid, and at the end of five days is quite transparent, when it is no longer coloured by iodine. Under the same conditions, solutions of amylopectin take a shorter, and of amylose a longer, time to become transparent. The transparent solution, when treated with ten volumes of alcohol, gives a precipitate having all the properties of an achroodextrin, the amount of which diminishes and has entirely disappeared at the end of the twelfth day. The same changes occur if the liquid is previously rendered slightly alkaline with sodium hydrogen carbonate. The course of the oxidation can be traced by withdrawing samples from the solution at intervals of twenty-four hours and estimating the acidity by titration with standard alkali, whilst the undecomposed hydrogen peroxide may be estimated with permanganate. To determine the reducing power towards Fehling's solution, the hydrogen peroxide is first decomposed by adding platinum black to the neutralised sample.

Examination of the curves tracing the rate of decomposition of the hydrogen peroxide shows that 5 c.c. of hydrogen peroxide decompose most rapidly in 100 c.c. of water, only traces remaining after ten days, less rapidly in a 1% glycogen solution, about 16% being left at the end of twenty-three days, and still less rapidly in a starch solution, 50% being still undecomposed after twenty-three days. In more concentrated solutions the decomposition is more rapid, probably owing to the greater acidity and different character of the colloid. The change in the reducing power of glycogen is slower, and in acidity is faster, than the corresponding changes for starch. Whilst the action of hydrogen peroxide on glycogen is more energetic than that on starch, the converse is true of the action of the amylase from the pancreatic juice of the dog on these two substances.

E. H.

**New Method of Preparation of Primary and Secondary Amines from Ketones.** KARL LÖFFLER (*Ber.*, 1910, 43, 2031—2035).—By the action of ammonia or methylamine on ketones and subsequent reduction with sodium ethoxide, primary and secondary amines are readily obtained in good yields. It is assumed that the imine,  $X_1X_2C:NR$ , is the intermediate product of the change being formed by elimination of water between ketone and ammonia, or from a ketoammonia compound. Thus from acetone and ammonia a mixture of isopropylamine and diisopropylamine is formed; the formation of the latter is explained as due to the isopropylamine formed reacting with unchanged acetone in the same manner. isoPropylamine aurichloride ( $H_2O$ ) forms matted plates, m. p. 72—73° [Fenner and Tafel (*Abstr.*, 1900, i, 111) give m. p. 131—135°, which probably refers to the nearly dry salt]. The aurichloride of di-isopropylamine separates in masses of intergrown needles, m. p. 169—170°.

sec.-Amylamine is obtained in the same way from methyl propyl ketone and ammonia; the platinichloride forms glistening plates, decomp. 215°; the normal oxalate has m. p. 226°; the sulphate crystallises in colourless plates.

E. F. A.

**Synthetic Homocholine.** FRIEDRICH KUTSCHER (*Zeitsch. physiol. Chem.*, 1910, 67, 296).—In reference to the work of Malengreau and



Lebailly on this subject (this vol., i, 545), it is pointed out that synthetic homocholine was prepared by Berlin in the author's laboratory, but his results are not yet published.

W. D. H.

**Additions to the Papers on  $\epsilon$ -Amino- $\alpha$ -guanidinohexoic Acid and New Syntheses of Amino-hydroxy-acids and of Piperidone Derivatives.** EMIL FISCHER and GÉZA ZEMPLÉN (*Ber.*, 1910, 43, 2189—2192. Compare this vol., i, 100, 305).—The dihydrochloride of an anhydride of  $\epsilon$ -amino- $\alpha$ -guanidinohexoic acid was obtained by the decomposition of  $\epsilon$ -benzoylamino- $\alpha$ -guanidinohexoic acid with hydrochloric acid. The free base,  $\epsilon$ -amino- $\alpha$ -guanidinohexoic anhydride,  $C_7H_{14}ON_4$ , is a colourless, crystalline powder, which turns bright red at 175—185°, and decomposes at 190° to a brownish-yellow liquid. The *platinichloride* is a yellow, crystalline powder, which becomes grey at 220—230°, and decomposes at 230—240°.

The amorphous compound obtained by the hydrolysis of gelatin, previously described as possessing some points of resemblance to the synthetic  $\beta$ -hydroxy- $\alpha$ -piperidone, is now found to be a mixture of anhydrides of  $\alpha$ -amino-acids.

E. F. A.

**Nitrogen and Sulphur Derivatives of Carbon Disulphide. XIV. Phosphorescence of Organic Sulphur Compounds by Spontaneous Oxidation.** MARCEL DELAPINE (*Bull. Soc. chim.*, 1910, [iv], 7, 722—724).—In addition to the compounds containing the group  $S:CO\cdot$  already described (this vol., i, 295), which are phosphorescent by spontaneous combustion, *methyl sulphocarbonic chloride*,  $Cl\cdot CS\cdot OMe$ , b. p. 107—108°, and *ethyl sulphocarbonic chloride*,  $Cl\cdot CS\cdot OEt$ , are observed to fume in the air and phosphoresce strongly with an ozone-like odour. When the methyl ester is treated with magnesium methyl iodide, it gives the compound,  $Me\cdot CS\cdot OMe$ , b. p. 87—89°, which also fumes and phosphoresces strongly. The only compound, not containing the above group, which oxidises with brilliant phosphorescence is carbon chlorosulphide,  $SCl_2$ . Methyl and ethyl methyl thiocarbonate,  $SMe\cdot CO\cdot OR$ , methyl ethyl thiocarbonate,  $SEt\cdot CO\cdot OMe$ ,

methyl dithiocarbonate,  $CO(SMe)_2$ , and methyl dimethothiocarbamate,  $SMe\cdot CO\cdot NMe_2$ , which contain the grouping  $O:CS\cdot$ , and the iminothiocarbonic esters,  $NMe\cdot C(SMe)\cdot OMe$ ,  $NMe\cdot C(SEt)\cdot OMe$ , and  $NEt\cdot C(SMe)\cdot OMe$ , which contain the grouping  $:C\begin{smallmatrix} O \\ \diagup \diagdown \\ S \end{smallmatrix}$  (see following

abstract), do not phosphoresce. Tetramethyl-, tetraethyl-, and tetrapropyl-isothiobarbitimides,  $NR\cdot C(SR)\cdot NR_2$ , and the isomeric tetra-alkylthiocarbamides,  $CS[NR_2]_2$ , which are formed by replacing the  $\cdot OR$ -group of the phosphorescent sulphocarbonic esters,  $NRR'\cdot CS\cdot OR$ , with the group  $\cdot NRR'$ , as well as the thiosulphocarbonic esters,

$NRR'\cdot CS\cdot SR'$ ,

are similarly inactive. The sulphocarbonic esters,  $NH_2\cdot CS\cdot OR$  or  $NHR'\cdot CS\cdot OR$ , which contain a hydrogen atom combined with the nitrogen, do not, unlike their alkyl derivatives, phosphoresce by spontaneous oxidation.

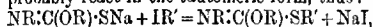
It is suggested that the readiness with which the compounds con-

taining the group  $S\cdot\dot{C}\cdot O\cdot$  are oxidised is due to the residual affinity of the sulphur and carbon atoms. E. H.

**Nitrogen and Sulphur Derivatives of Carbon Disulphide.**  
**XV. Iminothiocarbonic Esters of the Aliphatic Series:**  
 $RN:C(OR)(SR_1)$ . MARCEL DELÉPINE (*Bull. Soc. chim.*, 1910, [iv], 7, 724—727).—Some of the iminothiocarbonic esters, which contain the grouping  $C\begin{smallmatrix} S \\ \diagup \\ O \end{smallmatrix}$ , have been prepared for comparison with the

compounds (preceding abstract) containing the grouping  $S\cdot\dot{C}\cdot O\cdot$ , which are phosphorescent by spontaneous oxidation. Hitherto only the aromatic derivatives of this series have been prepared (compare Liebermann, *Abstr.*, 1882, 296; Wheeler and Dustin, *Abstr.*, 1901, i, 24).

When the sodium salts of the thiocarbamic esters prepared according to Roschdestvensky's method (this vol., i, 107) are treated with alkyl iodides they probably react in the tautomeric form, thus:



giving the aliphatic iminothiocarbonic esters. The latter are colourless, mobile liquids, boiling almost  $50^\circ$  lower than, and appreciably less dense than, the corresponding iminodithiocarbonic esters, which they resemble in colour. The iminothiocarbonic esters are weak bases, soluble in dilute acids, but readily displaced by alkalis or ammonia, neutral to litmus and phenolphthalein, but exactly mono-acid towards helianthin. They are hydrolysed by boiling dilute acids into the amine and thiocarbonic ester. The iminothiocarbonic esters, like the dithio-compounds, lose the  $\cdot SR'$  group when treated with silver nitrate or mercuric chloride.

Neither the iminothiocarbonic esters nor the sulphourethanes,  $NHR\cdot CS\cdot OR'$ , obtained intermediately, nor the thiocarbonic esters,  $CO(OR)(SR')$ , formed on hydrolysis, fume or phosphoresce when brought into contact with the air. The picrates of the first-named compounds form well-defined, yellow crystals.

*Dimethyl methyliminiothiocarbonate*,  $NMe:C(SMe)\cdot OMe$ , a liquid, b. p.  $142-144^\circ$ ,  $D_4^{20}$  1.0654,  $D_4^{25}$  1.0457,  $n_D^{20}$  1.48458, when hydrolysed gives the hitherto unknown *methyl methyl thiolcarbonate*,  $CO(SMe)\cdot OMe$ , which is a colourless liquid having an ethereal odour, b. p.  $120-121^\circ$ ,  $D_4^{20}$  1.1452,  $D_4^{25}$  1.1203,  $n_D^{20}$  1.45242; the *picrate* of the former has m. p.  $116^\circ$ .

*Methyl ethyl methyliminiothiocarbonate*,  $NMe:C(SEt)\cdot OMe$ , has b. p.  $158-160^\circ$ ,  $D_4^{20}$  1.0320,  $D_4^{25}$  1.0125,  $n_D^{20}$  1.48189; the *picrate* has m. p.  $100^\circ$ . *Dimethyl ethyliminiothiocarbonate*,  $NEt:C(SMe)\cdot OMe$ , has b. p.  $154-155^\circ$ ,  $D_4^{20}$  1.02545,  $D_4^{25}$  1.0056,  $n_D^{20}$  1.47838; the *picrate* has m. p.  $94^\circ$ . Instead of the values previously given, the author finds for dimethyl thioncarbonate,  $CS(OMe)_2$ ,  $D_4^{20}$  1.13065,  $D_4^{25}$  1.1028,  $n_D^{20}$  1.45962. The latter compound is distinguished from the isomeride,  $SMe\cdot CO\cdot OMe$ , by reacting immediately with silver nitrate, silver sulphide being precipitated. E. H.

**A Simple Method of Preparation of Pure Cyanamide.** FRITZ BAUM (*Biochem. Zeitsch.*, 1910, 26, 325—332).—Seventy-five grams of

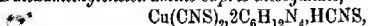
calcium nitride are stirred for half an hour with 400 c.c. of water. The process is repeated with a second quantity of water, which is finally used for treatment of a second batch of nitride. A third extract with water of the first batch is used for a second treatment of the second batch, and then for a first treatment of a third batch of nitride, etc. Finally, an extract is obtained which has been employed for treatment of four lots of nitride, and which is a strong solution of cyanamide. This is neutralised with sulphuric acid, separated from the precipitated calcium sulphate, and the liquid is then concentrated in a vacuum. On cooling, the residue crystallises, and the cyanamide is then separated from the calcium sulphate, and dicyandiamide formed as a by-product by extraction with ether. The ether is diluted, as another by-product is often precipitated which is not soluble in the dilute solution of cyanamide in ether. After distilling off the ether, pure cyanamide which distils at  $143-144^{\circ}/18$  mm., is obtained. On treatment with methyl alcohol and hydrochloric acid, it yields the methyl ether of isocarbamide.

S. B. S.

**Double Thiocyanates of Bivalent Copper and of Cobalt with Organic Bases.** J. CALZOLARI (*Ber.*, 1910, 43, 2217-2219).—Cupric thiocyanate, although insoluble in, and decomposed by, water, dissolves unchanged in concentrated solutions of an alkali thiocyanate. From the solution, however, thiocyanates of bivalent copper cannot be isolated, since they readily decompose, especially on warming, with the deposition of cuprous thiocyanate. The following double thiocyanates of bivalent copper with organic bases can, however, be readily isolated.

*Tripyridinium cupric thiocyanate*,  $\text{Cu}(\text{CNS})_2 \cdot 3\text{Py} \cdot \text{HCNS}$ , is obtained as a reddish-brown precipitate by adding a concentrated solution of copper nitrate to a saturated solution of ammonium thiocyanate until the black precipitate first formed redissolves, filtering, and then adding a concentrated solution of pyridine thiocyanate.

*Di-hexamethylenetetramine cupric thiocyanate*,



separates as a light green, crystalline precipitate when hexamethylenetetramine thiocyanate is used instead of pyridine thiocyanate. Since the compound is anhydrous, the green colour, which is different from the reddish-brown colour of the solutions of cupric thiocyanate in concentrated solutions of the alkali thiocyanates, must depend on the organic base. This is confirmed by the fact that *di-hexamethylenetetramine cobalt thiocyanate*,  $\text{Co}(\text{CNS})_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{HCNS}$ , which was prepared in a similar manner to the corresponding copper compound, forms lilac-coloured crystals, whereas the thiocyanates of cobalt are blue.

*Hexamethylenetetramine thiocyanate* is precipitated from a saturated solution of ammonium thiocyanate (1 mol.) and hexamethylenetetramine (1 mol.) on the addition of hydrogen chloride; it forms large, transparent, colourless, monoclinic prisms.

T. S. P.

**Crystallographical and Optical Investigations of Organic Compounds.** C. BLASS (*Zeitsch. Kryst. Min.*, 1910, 48, 20-44).—The following crystallographic determinations are given: Potassium

molybdenum hexathiocyanate, pseudohexagonal [ $a:c=1:0.67197$ ]; the ammonium salt, rhombic [ $a:b:c=0.60721:1:0.88406$ ], and the sodium salt, triclinic [ $b:c=1:0.98114$ ]. Potassium chromihexathiocyanate, pseudohexagonal [ $a:c=1:0.67934$ ], the ammonium salt, rhombic [ $a:b:c=0.61109:1:0.87651$ ], and the sodium salt, triclinic.

Corydine is tetragonal trapezohedric [ $a:c=1:0.39896$ ], and has  $[\alpha]_D^{20} + 204.35^\circ$  in chloroform; bulbocapnine, rhombic hemihedral [ $a:b:c=0.72520:1:0.71792$ ],  $[\alpha]_D^{20} + 237.1^\circ$  in chloroform; bulbocapnine monomethyl ether, tetragonal hemihedral [ $a:c=1:1.05540$ ],  $[\alpha]_D^{20} + 247.2^\circ$  in chloroform; monobenzoylbulbocapnine, rhombic [ $a:b:c=0.89437:1:0.63116$ ],  $[\alpha]_D^{20} + 92.7^\circ$  in chloroform; ephedrine-phenylthiocarbamide, rhombic hemihedral sphenoidal [ $a:b:c=0.81703:1:0.42834$ ],  $[\alpha]_D^{20} - 105.1^\circ$  in abs. alcohol;  $\psi$ -ephedrine-thiocarbamide, rhombic [ $a:b:c=0.37134:1:0.62669$ ],  $[\alpha]_D^{20} + 22.8^\circ$  in absolute alcohol.

Patchouli-alcohol, hexagonal [ $a:c=1:0.56528$ ],  $[\alpha]_D^{20} - 124.5^\circ$  in alcohol; cedrol, rhombic [ $a:b:c=0.98385:1:0.70502$ ],  $[\alpha]_D^{20} - 84^\circ$  to  $-61^\circ$ ; cypress camphor, rhombic [ $a:b:c=0.98844:1:0.71772$ ], is optically inactive; guaiol (chamapcol), trigonal pyramidal [ $a:b:c=1:0.54959$ ],  $[\alpha]_D^{20} - 29.8^\circ$ ; benzoyl-eugenol, monoclinic [ $a:b:c=1.5829:1:1.0713$ ]; acetyliso-eugenol, rhombic [ $a:b:c=0.68815:1:0.97672$ ]; isopirle, monoclinic [ $a:b:c=0.876502:1:1.7878$ ]; menthyl benzoate, rhombic [ $a:b:c=0.76134:1:0.24476$ ],  $[\alpha]_D^{20} - 90.72^\circ$ ; guaiol-glycerol, rhombic [ $a:b:c=0.23916:1$ ].

$\alpha$ -Methyl- $\alpha$ -ethylpiperidine, rhombic [ $a:b:c=0.6777:1:0.61179$ ].

T. S. P.

**The Destruction of Cyanide.** JAMES MOIR and JAMES GRAY (*Chem. Met. Min. Soc. S.A.*, 1910, 10, 433-441).—Experiments are described which had for their object the destruction of cyanide. Complete destruction can be achieved by several methods (such as the action of silver and cuprous salts and of ammonium disulphide), but the ferrocyanide reaction is the only one which would be commercially successful on the Rand. A thorough investigation of this reaction showed (1) that when *excess* of alkali is used, the amount of ferrocyanide formed is less than when smaller quantities of alkali are present; (2) that rise of temperature above  $20^\circ$  is harmful to the reaction; (3) that the results are nearly independent of dilution; (4) that the reaction is as complete in five to ten seconds as after a long time, and (5) that unless the alkalinity is most carefully adjusted to suit the amount of iron used, an excess of ferrous solution gives no better results than the theoretical quantity (that required by the equation:  $6\text{KCN} + 2\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \text{K}_2\text{Fe}[\text{CN}]_6 + 2\text{K}_2\text{SO}_4 + 7\text{H}_2\text{O}$ ).

In no case have the authors succeeded in obtaining entire destruction of the cyanide used, although in several cases they obtained a reaction sufficiently complete for all industrial purposes, the cyanide having been reduced to three or four parts per million.

It is pointed out that a solution containing free hydrocyanic acid cannot be correctly estimated with silver nitrate; for correct results it is necessary to add an excess of alkali before titration with the silver nitrate.

T. S. P.

**Perylene, a Highly Condensed Aromatic Hydrocarbon,**  $C_{20}H_{12}$ . ROLAND SCHOLL, CHRISTIAN SEER, and RICHARD WEITZENBÖCK (*Ber.*, 1910, 43, 2202—2209).—Scholl and Mansfeld (this vol., i, 494) have shown that *meso*-benzdianthrone, when heated at 140—145° with anhydrous aluminium chloride, is converted into *meso*-naphthodianthrone. By the same reaction the hydrocarbon  $C_{20}H_{12}$  (annexed formula) is obtained from 1:1'-dinaphthyl and also directly from naphthalene. To establish the constitution as a *peri*-derivative, 1:8-naphthalenediamine was converted into the azimide, this into 8-*iodo-naphthylamine*, and further into 1:8-di-*iodonaphthalene*, which last when heated with copper powder yielded the above hydrocarbon, *peri-dinaphthulene*, which it is proposed to term perylene. Perylene forms glistening yellow or bronze-hued, crystalline plates, m. p. 264—265°, and gives yellow or reddish-yellow solutions with a brilliant blue fluorescence.

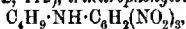
8-*Iodo-naphthylamine* forms colourless needles, m. p. 82°; the *hydrochloride* forms grey needles, which darken at 170°, m. p. 186—189° (decomp.). 1:8-Di-*iodonaphthalene* forms bright brown needles, m. p. 109°.

*Dibenzoylperylene*, prepared by the action of benzoyl chloride and aluminium chloride on perylene, was obtained in yellow crystals, m. p. 280—285°; the xylene solution shows a green fluorescence.

E. F. A.

**Monoalkylnitroamines.** ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], 14, 296—312. Compare *Abstr.*, 1898, i, 9).—Contrary to the observations of Simon Thomas (*Abstr.*, 1891, 167), the author finds that picryl chloride in alcoholic solution reacts with the potassium salts of ethyl- and propyl-nitroamine, giving respectively trinitrophenyl-ethyl- and -propyl-nitroamines. The yield of trinitrophenylethylnitroamine amounts to almost 90% of theory, but in the second reaction only about two-thirds of the picryl chloride is decomposed, a mixture of almost equimolecular quantities of potassium chloride and picrate being precipitated, whilst the unattacked picryl chloride will react with a further amount of potassium propylnitroamine. Similarly, potassium butylnitroamine when treated with picryl chloride gives a small quantity of *trinitrophenylbutylnitroamine*,  $C_6H_2N(NO_2)_3 \cdot C_4H_9$ , which forms almost colourless, nacreous spangles, m. p. 98—99°, together with much potassium picrate.

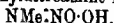
This compound can also be prepared by van Romburgh's method (*Rec. trav. chim.*, 1883, 2, 112), *trinitrophenylbutylamine*,



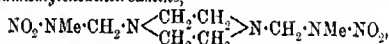
which crystallises in long, slender, orange-yellow needles, m. p. 80.5—81°, being an intermediate product.

The decreasing yield of aliphatic trinitrophenylnitroamine, obtained on ascending the series of aliphatic nitroamines, is probably due to the increasing degree of dissociation of the potassium salts of the latter, and thus supports Simon Thomas's conclusion that methylnitroamine has a more strongly acid character than that possessed by its homologues.

Attempts to prepare acetyl or benzoyl derivatives of methylnitroamine failed (compare Simon Thomas, *loc. cit.*). With benzoyl chloride alone, or in the presence of benzene, methylnitroamine gives nitrous oxide, methyl chloride, and benzoic acid. Addition of benzoyl chloride to a mixture of the silver derivative of methylnitroamine with sand causes a violent explosion. The reaction with benzoyl chloride is explicable on the assumption that methylnitroamine has the constitution



The nitroamine is perhaps transformed into the latter under the influence of substances with which it reacts, thus the salts of *o*- and *p*-nitrophenol and of carbonic, hydrocyanic, cyanic, sulphydric, sulphurous, and nitrous acids are decomposed by it, but it does not combine directly with aromatic amines, although it does so with ammonia. This constitution is also supported by the observation that methylnitroamine combines with piperidinomethyl alcohol and with piperazine. In the former case, large, colourless crystals, *m. p.* 52°, of *piperidinemethylnitroaminomethane*,  $\text{NO}_2\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}$ , are produced. This compound is unstable, and dissolves slowly with decomposition in cold water. Butylnitroamine reacts with piperidinomethyl alcohol, giving a liquid product, whilst ethylenedinitroamine forms magnificent crystals, *m. p.* 123°, of *piperidine-ethylenedinitroaminomethane*,  $\text{C}_2\text{H}_4[\text{N}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_{10}]_2$ , which behave similarly to the methyl derivative. With piperazine, methylnitroamine forms *piperazinedimethylenedinitroamine*,



which crystallises in nacreous leaflets, decomposing at 170°.

The latter compounds react as though they possess the constitution  $\text{R}\cdot\text{N}\cdot\text{NO}\cdot\text{OR}'$ ; nevertheless, in previous communications (Abstr., 1899, i, 106), reactions in support of the formula  $\text{CH}_3\cdot\text{NH}\cdot\text{NO}_2$  for methylnitroamine have been described.

E. H.

**Trinitrophenylalkylnitroamines.** ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], 14, 313—314).—The alkylpicramides,  $\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{NHR}$ , are yellow or orange-coloured substances, whilst the trinitrophenylalkylnitroamines are only very faint yellow, but are coloured purple-red by alkalis.

The author considers that the difference in colour between the two classes of compounds is related to the replacement of the imide hydrogen by the nitro-group, and points out that this is in accordance with the views recently expressed by Hantzsch (this vol., i, 475). The coloration of the trinitrophenylalkylnitroamines by alkalis is perhaps due to the conjugation of two nitro-groups with the metal or ammonia (compare Hantzsch and Picton, Abstr., 1909, i, 467).

E. H.

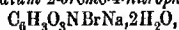
**Homochromoisomerism.** MAX BUSCH (*Ber.*, 1910, 43, 2070. Compare Hantzsch, this vol., i, 474).—Polemical. Busch and Pungs (Abstr., 1909, i, 564) were the first to recognise the two isomerides of picrylmethylaniline, and to carry out the mutual interconversion.

E. F. A.

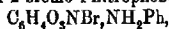
**Products of the Bromination of *o*- and *p*-Nitrophenol.** HENRI VAN ESP (*Rec. trav. chim.*, 1910, [ii], 14, 187—237).—The author has studied the preparation of 4-bromo-, 6-bromo- and 4:6-dibromo-2-nitrophenol, 2-bromo- and 2:6-dibromo-4-nitrophenol, 4-bromo-2:6-dinitrophenol, and 2-bromo-4:6-dinitrophenol. A résumé of the literature relative to each of these compounds is given. The following new compounds are described. *Calcium 4-bromo-2-nitrophenoxide*,  $(C_6H_3O_3NBr)_2Ca \cdot 2H_2O$ , forms a bright orange precipitate composed of microscopic needles; 4-bromo-2-nitrophenyl acetate, prepared from the phenol by means of acetic anhydride containing a small quantity of sulphuric acid, crystallises in very brilliant, colourless, triangular plates, m. p. 74.5—74.75°. By treating the product of the bromination of *o*-nitrophenol with aniline, the author separated a small quantity of 6-bromo-2-nitrophenol, which has not hitherto been prepared in this way. *Barium 4:6-dibromo-2-nitrophenoxide*,  $(C_6H_3O_3NBr)_2Ba \cdot 2H_2O$ , forms thin, doubly-refracting, orange needles; the *additive* compound of 4:6-dibromo-2-nitrophenol and aniline,  $NO_2 \cdot C_6H_2Br_2 \cdot OH \cdot NH_2 \cdot Ph$ , a crystalline, yellow powder, m. p. 87° (variable), easily breaks down into its components. If 4:6-dibromo-2-nitrophenol is left in contact with nitric acid (D 1.41) for some months, it is converted into 2-bromo-4:6-dinitrophenol, of which the *aniline* derivative has m. p. 151°. For 4-bromo-2:6-dinitrophenol the author finds m. p. 74.5°, whilst Körner (*Zeit. Chem.*, 1868, 4, 322) and Armstrong and Prevost (*Trans.*, 1875, 28, 520; *Abstr.*, 1874, 1164) give 78°, and Austen (*Jahresber.*, 1878, i, 550) gives 71°.

*Potassium 4-bromo-2:6-dinitrophenoxide*,  $C_6H_3O_3N_2BrK$ , is a blood-red substance; the *sodium* salt,  $C_6H_3O_3N_2BrNa \cdot 2H_2O$ , forms thin, doubly-refracting needles of the same colour; the *barium* and *calcium* salts,  $(C_6H_3O_3N_2Br)_2Ca \cdot 2H_2O$ , crystallise in bright yellow needles. The *additive* compound of 4-bromo-2:6-dinitrophenol and aniline,  $C_6H_3O_3N_2Br \cdot Ph \cdot NH_2$ , is an orange, microcrystalline powder, m. p. 137.5—137.75°, sufficiently stable to be recrystallised from warm water; 4-bromo-2:6-dinitrophenyl acetate crystallises in brilliant doubly-refracting, colourless, orthorhombic prisms, m. p. 110.5°, which became yellowish-brown in moist air.

By the bromination of *p*-nitrophenol, previous workers have obtained 2-bromo-4-nitrophenol with too low a m. p. (102°). This is shown to be due to admixture with dibromonitrophenol, which cannot be removed by recrystallisation of the phenol or of its barium or potassium salt. By treating the benzene solution of the bromination product with aniline, the dibromonitrophenol is precipitated in the form of its aniline derivative. Pure 2-bromo-4-nitrophenol can be obtained from the filtrate in crystals, m. p. 112.25°. The presence of hydrobromic acid inhibits the formation of the dibromo-compound to a certain extent. *Sodium 2-bromo-4-nitrophenoxide*,



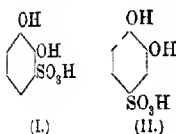
and the *potassium* salt ( $1\frac{1}{2}H_2O$ ) crystallise in radial groups of microscopic, bright yellow, doubly-refracting, pointed needles; the *calcium* salt forms a microcrystalline powder composed of thin needles; the *additive* compound of 2-bromo-4-nitrophenol and aniline,



forms greenish-yellow crystals, m. p. 55—69°, which lose aniline

completely when exposed over sulphuric acid in a vacuum; 2-bromo-4-nitrophenyl acetate crystallises in irregular, birefracting, colourless prisms, m. p. 61.75°. For 2:6-dibromo-4-nitrophenol the author observed the m. p. 143°, and, contrary to the statements of previous workers, found that it was not decomposed at 180°. Sodium 2:6-dibromo-4-nitrophenoxide,  $C_6H_2O_3NBr_2Na$ , crystallises above 50° with  $2H_2O$  in deep orange crystals, and below 20° with  $5H_2O$  in yellow crystals; the calcium salt,  $(C_6H_2O_3NBr_2)_2Ca \cdot 4H_2O$ , crystallises in irregular, doubly-refracting, orange-coloured rhombs; the additive compound of 2:6-dibromo-4-nitrophenol and aniline,  $C_6H_2O_3NBr_2 \cdot NH_2Ph$ , forms slender, yellow needles, m. p. 155.5°, which give almost colourless solutions in neutral solvents and only lose aniline very slowly when boiled with water. Potassium 2-bromo-4:6-dinitrophenoxide crystallises with  $1H_2O$ ; the additive compound of 2-bromo-4:6-dinitrophenol and aniline,  $C_6H_3O_3N_2Br \cdot NH_2Ph$ , forms slender, yellow needles, m. p. 151°, and can be recrystallised from boiling water; 2-bromo-4:6-dinitrophenyl acetate forms short, stout, doubly refracting, colourless, rhombohedral crystals, m. p. 104.5° E. H.

Catecholmonosulphonic Acid. CURT GENTSCH (*Ber.*, 1910, 43, 2018—2020).—Cousin (Abstr., 1893, i, 637) considered the catechol-sulphonic acid, which he obtained by sulphonating catechol below 100°, to be an ortho-



acid of constitution (I), and isomeric with the para-acid (II) described by Barth (Abstr., 1879, 933). It is shown that the two acids are identical, both forming a characteristic barium salt ( $4H_2O$ ) crystallising in rosettes of rectangular prisms, whilst Cousin's acid gives 1:2-dimethoxybenzene-4-sulphonic acid (compare Paul, Abstr., 1906, i, 843) on methylation. It must accordingly be removed from the literature. E. F. A.

Simple Formation of Benzyl Ethers. HANS VON HALBAN (*Ber.*, 1910, 43, 2071. Compare Braun, this vol., i, 479).—Polemical. The fact that benzyl halogenides react with alcohol, forming ethers, has already been observed (compare Abstr., 1909, ii, 722). Benzyl halogenides also react with phenols and carboxylic acids. E. F. A.

Preparation of Aromatic Alcohols and their Acetates. ALFRED WOHL and ERICH BERTHOLD (*Ber.*, 1910, 43, 2175—2185).—Grignard (Abstr., 1904, i, 494) has described the preparation of phenylethyl alcohol by the following series of reactions:

$$CH_3Br \cdot CH_2Br \rightarrow CH_3Br \cdot CH_2 \cdot OPh,$$

$$CH_3Ph \cdot CH_2 \cdot OPh \rightarrow CH_3Ph \cdot CH_2Br \rightarrow CH_3Ph \cdot CH_2 \cdot OH,$$

and the authors have re-examined these reactions in detail. A 59% yield of pure  $\omega$ -bromophenetole can be obtained by gradually adding 4*N*-sodium hydroxide solution to a mixture of ethylene dibromide, phenol, and water heated in an oil-bath at 100—105°, and kept well stirred. A 48.4% of  $\omega$ -chlorophenetole can be obtained by a similar method, using ethylene dichloride, a shaking apparatus, and a tem-



perature of  $110^{\circ}$ .  $\beta$ -Naphthol gives a 40% yield of its  $\omega$ -bromoethyl ether (Kolbe, Abstr., 1881, 177). Eugenole gives a 25% yield of the bromoethyl ether,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , which has m. p.  $26-27^{\circ}$  and b. p.  $160-170^{\circ}/7$  mm.

*Guaiacol  $\omega$ -bromoethyl ether*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$  (40% yield), has m. p.  $43-45^{\circ}$  and h. p.  $135-140^{\circ}/7$  mm.

*Phenyl vinyl ether*,  $\text{CH}_2\text{:CH}\cdot\text{OPh}$ , obtained by heating  $\omega$ -bromophenetole with twice its weight of anhydrous potassium hydroxide in a copper flask, is a colourless liquid, b. p.  $155-156^{\circ}$ . A by-product is *diphenoxyethyl ether*,  $\text{O}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh})_2$ , which crystallises from dilute alcohol in colourless needles, m. p.  $66-67^{\circ}$ . *Eugenyl vinyl ether*,  $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2$  (50% yield), is a mobile liquid, b. p.  $260-262^{\circ}$ , and *guaiacyl vinyl ether* (50% yield) has b. p.  $202-203^{\circ}$ .

$\omega$ -Bromophenetole, bromobenzene, and sodium powder in the presence of ether yield phenol, ethylene, and unaltered bromobenzene.

A 71% yield of  $\omega$ -phenylphenetole is obtained by the action of magnesium phenyl bromide on  $\omega$ -bromophenetole in the presence of xylene at  $150-155^{\circ}$ , and when this is hoiled with glacial acetic acid and 70% sulphuric acid, a 65% yield of phenylethyl acetate is obtained.

A 38% yield of phenylethyl alcohol can be obtained by the action of nitrous acid on  $\beta$ -phenylethylamine.

*Phenylmethylvinyl acetate*,  $\text{CMePh}\cdot\text{CH}\cdot\text{OAc}$ , obtained by boiling hydratropaldehyde with acetic anhydride and two drops of concentrated sulphuric acid, is a clear, colourless liquid, b. p.  $120-122^{\circ}/8-9$  mm., and when reduced with hydrogen and platinum black yields  $\beta$ -phenylpropyl acetate,  $\text{CHMePh}\cdot\text{CH}_2\cdot\text{OAc}$ , with b. p.  $103-105^{\circ}/10$  mm.

J. J. S.

**Fixation of Trioxymethylene by Magnesium Derivatives of the Homologues of Benzyl Bromide.** PAUL CARRÉ (*Compt. rend.*, 1910, 151, 149-151.\* Compare Abstr., 1909, i, 544).—Trioxymethylene reacts with magnesium mesityl bromide in the same way as with magnesium benzyl chloride (Tiffeneau, Abstr., 1904, i, 46), forming *s*-mesitylcarbinol,  $\text{C}_6\text{H}_3\text{Me}_3\cdot\text{CH}_2\cdot\text{OH}$ , needles, m. p.  $88-89^{\circ}$ , h. p.  $140-141^{\circ}/15$  mm.; the *phenylurethane* crystallises in long prisms, m. p.  $124-125^{\circ}$ . The product of the reaction also contains *s*-dixylylethane (Moritz, Abstr., 1899, i, 910), mesitylene, and *s*-dixylyldimethyl ether,  $\text{O}(\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Me}_3)_2$ , silky needles, m. p.  $148^{\circ}$ . The constitution of the latter follows from its conversion by hydrogen bromide into 2:4:6-trimethylbenzyl bromide,  $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CH}_2\text{Br}$ , long tablets, m. p.  $52^{\circ}$ , which yield *s*-mesitylcarbinol on hydrolysis.

Wispek's *s*-xylylacetic acid has m. p.  $103^{\circ}$  (Abstr., 1883, 1095); it could not be detected amongst the products of the foregoing reaction. The ethyl ester has b. p.  $141-142^{\circ}/18$  mm., and on reduction forms *s*-xylylethanol, a mobile liquid having a rose-like odour, b. p.  $134-135^{\circ}/15$  mm.; the *phenylurethane* crystallises in long prisms, m. p.  $90^{\circ}$ ; the acetate has b. p.  $138-139^{\circ}/13$  mm.

W. O. W.

**Crystalline Form of Cholesteryl Salicylate.** EYDOR ARISI (*Atti R. Acad. Lincei*, 1910, [v], 19, i, 782-784).—Cholesteryl

\* and *Bull. Soc. chim.*, 1910, [iv], 7, 841-846.

salicylate,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{C}_{27}\text{H}_{45}$ , prepared by fusing cholesterol and salicylic acid at  $170^\circ$ , melts at  $180^\circ$ , and has  $[\alpha]_D^{20} - 53.78^\circ$  in chloroform solution. The crystals are small, but distinctly formed, and are triclinic [ $a:b:c = 0.77364:1:0.50407$ ;  $a = 92^\circ 55' 24''$ ,  $\beta = 101^\circ 58' 32''$ ,  $\gamma = 95^\circ 14' 10''$ ]. C. H. D.

*pp*-Dibromobenzhydrol. A Correction. HEINRICH BILTZ (*Ber.*, 1910, 43, 2263. Compare this vol., i, 570).—The compound, m. p.  $174-175^\circ$ , obtained by the decomposition of dibromobenzilic acid, and described as dibromobenzhydrol, is in reality di-*p*-bromobenzophenone. E. F. A.

Condensation of Ethyl Nitrate with *o*-Bromophenylacetonitrile. WILHELM WISLICENUS and MAX FISCHER (*Ber.*, 1910, 43, 2234—2243).—Ethyl nitrate condenses with *o*-bromophenylacetonitrile in presence of sodium ethoxide less readily than with the corresponding *p*-compound (*Abstr.*, 1909, i, 29). In presence of potassium ethoxide the potassium salt of *o*-bromo-*o*-isonitrophenylacetonitrile,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{ON})\cdot\text{NO}_2\text{K}$ , is obtained. Nitrous acid is readily eliminated from the free compound to form *oo'*-dibromo-*aa'*-dicyanostilbene. The isonitro group is more stable in alkaline solution; on boiling, cyanide is eliminated and *o*-bromo-*o*-nitrotoluene formed. Stronger heating causes the elimination of the oximino-group also, and *oo'*-dibromostilbene is obtained. Sodium hydroxide and hydrogen peroxide convert the cyano-group into carbonamide. Treatment with bromine and subsequent elimination of nitric oxide and bromine leads to *o*-bromophenylacetonitrile. On reduction, *o*-bromo- $\alpha$ -aminophenylacetic acid is obtained.

*o*-Bromophenylacetonitrile boils without decomp. at  $145-147^\circ/13$  mm.

Sodium *o*-bromo-*o*-isonitrophenylacetonitrile crystallises in colourless plates, m. p.  $283-285^\circ$  (decomp.), and explodes on further heating. The potassium salt forms colourless, glistening plates. Both salts dissolve in water with a neutral reaction, the solution having a sweet taste. It gives neither coloration nor precipitate with ferric chloride, but the alcoholic solution becomes a deep brownish-red with this reagent.

The free *o*-bromo-*o*-isonitrophenylacetonitrile forms faintly yellow-coloured, pyramidal prisms, m. p.  $51-52^\circ$ , and gives an intense red coloration with ferric chloride in alcoholic solution. The methyl ether is colourless, m. p.  $104-105^\circ$ .

*oo'*-Dibromo-*aa'*-dicyanostilbene,  $[\text{C}_6\text{H}_4\text{Br}\cdot\text{C}(\text{CN})]_2$ , crystallises in colourless needles, m. p.  $145^\circ$ .

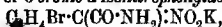
*o*-Bromo-*o*-nitrotoluene crystallises in colourless needles, m. p.  $55-56^\circ$ , and shows no ferric chloride reaction.

*oo'*-Dibromostilbene is obtained in colourless, lustrous plates, m. p.  $206-208^\circ$ ; the dibromide forms colourless needles, m. p.  $225^\circ$ .

*o*-Bromophenylacetonitrile was obtained in almost colourless, long, flat, glistening needles, m. p.  $65-67^\circ$  (Russanoff:  $62-64^\circ$ ). It reacts in ethereal solution with phenylhydrazine, forming *o*-bromobenzophenylhydrazide, which crystallises in needles, m. p.  $190-198^\circ$ .

*o*-Bromo- $\alpha$ -aminophenylacetic acid,  $C_6H_4Br \cdot CH(NH_2) \cdot CO_2H$ , separates in leaflets, which sublime at  $220-225^\circ$ , m. p.  $221^\circ$  (in closed tube).

The potassium salt of *o*-bromo- $\alpha$ -isonitrophenylacetamide,



crystallises in long, faintly yellow-coloured needles, decomp.  $246^\circ$ . On treatment with bromine, *o*:*o*-dibromo- $\alpha$ -nitrophenylacetamide is produced in colourless, microscopic prisms, m. p.  $156-157^\circ$  (decomp.).

E. F. A.

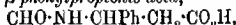
**Action of Benzaldehyde on the Monosodium Derivative of Phenylacetoneitrile.** F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1910, [iv], 7, 735-736).—When the monosodium derivative of phenylacetoneitrile in ethereal solution is treated with benzaldehyde the product consists of a mixture of substances. From the latter the only definite compound that can be isolated is  $\alpha$ -phenylcinnamoneitrile,  $CHPh : CPh \cdot CN$ , already described by Meyer, Janssen, Neura, and Frost (*Abstr.*, 1889, 596, 597).

The nitrile is probably formed by the reactions:  $Ph \cdot CHO + Ph \cdot CHNa \cdot CN = Ph \cdot CH(ONa) \cdot CHPh \cdot CN$ ;  $Ph \cdot CH(ONa) \cdot CHPh \cdot CN = NaOH + CHPh : CPh \cdot CN$ . Sodium benzoate, formed probably by a secondary reaction, is found in the aqueous liquor from which the above crude product is separated.

E. H.

**The Walden Inversion. V. Optically Active  $\beta$ -Amino- $\beta$ -phenylpropionic Acid.** EMIL FISCHER, HELMUTH SCHIEBLER, and REINHART GROH (*Ber.*, 1910, 43, 2020-2030. Compare *Abstr.*, 1909, i, 359).—The formyl compound of  $\beta$ -amino- $\beta$ -phenylpropionic acid has been resolved by means of quinidine and quinine into the optically active forms. By treatment with nitrous acid, these were converted into the corresponding hydroxy-acids, but the change is accompanied by racemisation, due to the influence of the direct attachment of the phenyl to the asymmetric carbon atom. Enough activity remains, however, to identify the hydroxy-acids with those obtained by McKenzie and Humphries (*Trans.*, 1910, 97, 121). *d*- $\beta$ -Amino- $\beta$ -phenylpropionic acid gives *l*- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid. In the case of the ethyl ester of the amino-acid, the racemisation is less, and the hydroxy-acid rotates in the same direction, so that no Walden change takes place.

*dl*- $\beta$ -Formylamino- $\beta$ -phenylpropionic acid,



forms large, colourless prisms, which soften at  $125^\circ$ , m. p.  $123-123^\circ$  (corr.), to a colourless liquid. By means of the quinidine salt, *d*- $\beta$ -formylamino- $\beta$ -phenylpropionic acid was obtained in aggregates of microscopic, short needles, which soften at  $138^\circ$ , m. p.  $142-143^\circ$ ,  $[\alpha]_D^{20} + 116.4^\circ$  ( $\pm 0.2^\circ$ ). The quinine salt yields the corresponding *l*-isomeride, which is very similar;  $[\alpha]_D^{20} - 114.4^\circ$  ( $\pm 0.2^\circ$ ). *d*- $\beta$ -Amino- $\beta$ -phenylpropionic acid, obtained by heating the formyl compound with 10% hydrochloric acid, crystallises in stout plates, m. p.  $234-235^\circ$  (decomp.), and has  $[\alpha]_D^{20} + 6.9^\circ$  in water,  $-1.3^\circ$  in *N*-hydrochloric acid,  $-9.1^\circ$  in *N*-sodium hydroxide. The *l*-isomeride is precisely similar in crystalline form, and has  $[\alpha]_D^{20} - 7.5^\circ$  in water,  $+1.3^\circ$  in *N*-hydrochloric acid,  $+8.9^\circ$  in *N*-sodium hydroxide. The copper salt crystallises in

*Ethyl d-β-amino-β-phenylpropionate* is a viscid oil, b. p. 155° (corr.)/13 mm.,  $D_{20}^{25}$  1.063,  $[\alpha]_D^{25} + 13.74^\circ (\pm 0.02^\circ)$ . The *l*-isomeride was prepared from partially racemised material, and had  $[\alpha]_D^{25} - 8.09^\circ (\pm 0.04^\circ)$ .

Conversion of the *d*-β-aminophenylpropionic acid into the hydroxy-acid gave a product, m. p. 96–98°;  $[\alpha]_D^{25} - 3.3^\circ$ , whereas McKenzie and Humphries (*loc. cit.*) found  $[\alpha]_D^{25} - 18.9^\circ$ . Similarly, the *l*-acid yields an hydroxy-acid; m. p. 94–96°;  $[\alpha]_D^{25} + 3.2^\circ$ .

*Ethyl d-β-aminophenylpropionate* yields the hydroxy-acid;  $[\alpha]_D^{25} - 3.5^\circ$ , rising to  $-6.4^\circ$  on crystallisation. E. F. A.

**Action of Estere of Monobasic Aliphatic Acids on the Sodium Derivative of Phenylacetoneitrile.** F. BODROUX (*Compt. rend.*, 1910, 151, 234–236,\* Compare Walther and Schickler, *Abstr.*, 1897, i, 522).—Sodamide was added to phenylacetoneitrile dissolved in dry ether, and an alkyl ester added to the resulting sodium derivative. The following compounds were prepared in this way: *α*-Cyanophenylacet-aldehyde,  $\text{CN}\cdot\text{CHPh}\cdot\text{CHO}$ , m. p. 157–158°, from ethyl formate, which on benzoylation gave Walther's enolic benzoyl derivative, m. p. 119°. Amyl formate gave the same compound in diminished yield (50%). Ethyl acetate formed *α*-cyanobenzyl methyl ketone,  $\text{CN}\cdot\text{CHPh}\cdot\text{COMe}$ , large prisms, m. p. 90°. *α*-Cyano-*α*-phenylbutan-β-one has m. p. 73° (Walther and Schickler give m. p. 58°). The foregoing compounds are easily hydrolysed by dilute alkalis, regenerating phenylacetoneitrile.

W. O. W.

**Tetrahydroellagic Acid.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1910, 43, 2016–2017. Compare this vol., i, 889).—The tetrahydroellagic acid described by Oser and Böker (*Abstr.*, 1890, 394), crystallising from pyridine in small, yellow needles, is in reality ellagic acid.

The isomeric tetrahydroellagic acid of Oser and Kalmann (*Abstr.*, 1881, 815), obtained in small, silky needles by fusing ellagic acid with potassium hydroxide, is in reality pentahydroxydiphenylmethyllolide,  $\text{C}_{15}\text{H}_8\text{O}_7$ .

E. F. A.

**The Beckmann Rearrangement.** PIETER J. MONTAGNE (*Ber.*, 1910, 43, 2014–2016).—Schroeter (*Abstr.*, 1909, i, 617) has explained the Beckmann rearrangement on the assumption of the formation of an additive product with hydrogen chloride, and the conversion of this into a compound with a univalent nitrogen atom,  $\text{R}_2\text{CCl}\cdot\text{N}<$ . It is pointed out that in the case of the ketoximes,  $\text{RR}'\text{C}:\text{N}\cdot\text{OH}$ , the additive product and the unsaturated compound cannot be intermediate compounds. Wallach (*Abstr.*, 1906, i, 522) has assumed the elimination of subsequent addition of hydrogen chloride. If this were so, the benzene nucleus, after the rearrangement, must be combined with a different carbon atom than before, which was shown not to be the case (compare Montagne, *Abstr.*, 1907, i, 140, 854).

E. F. A.

**Isomerism and Polymorphism. I. Ketones of the Type of enzylienedeoxybenzoin and their Interconversion by Heat, Light, and Other Agencies.** HANS STOSBE and FORSYTH J. WILSON (*Annalen*, 1910, 374, 237–287).—The isomerism of the benzylidene-

\* and *Bull. Soc. chim.*, 1910, [iv], 7, 848–852.

deoxybenzoin described by Stobbe and Niedenzu (*Amer.*, 1902, i, 103) has been more thoroughly studied in the cases of the ketones obtained from the three nitrobenzaldehydes and from piperonal.

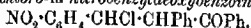
Hydrogen chloride is passed for six hours into an ethereal solution of deoxybenzoin and *o*-nitrobenzaldehyde at 0°; after being kept for three days at this temperature, the solution deposits white and yellow crystals. The former, after recrystallisation from benzene, have m. p. 132—133°, and consist of *chloro-o-nitrobenzyldeoxybenzoin*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}\cdot\text{CHPh}\cdot\text{COPh}$ , which is an unstable substance, being converted into the *ether*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OEt})\cdot\text{CHPh}\cdot\text{COPh}$ , m. p. 128—129°, by boiling alcohol, and losing hydrogen chloride by keeping in the air or in benzene or ethereal solution, or, best, by heating with aniline, yielding the yellow crystals, which consist of *o-nitrobenzylidenedeoxybenzoin*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CPh}\cdot\text{COPh}$ , m. p. 120—121°. This unsaturated ketone is converted into a paler yellow isomeride, *iso-o-nitrobenzylidenedeoxybenzoin*, m. p. 109—110°, by an exposure to sunlight for three months of its benzene solution containing a little iodine, by passing hydrogen chloride into its benzene solution for a few minutes, and then keeping for eleven hours, or by the action of sunlight on the powdered crystals; in each case a mixture of the two isomerides is produced, which is separated by means of alcohol. The *iso*-compound is more easily converted into the other, the change proceeding to the extent of 50% by exposing its benzene solution containing iodine to sunlight for five days, or by keeping its benzene solution, containing hydrogen chloride, for a week. Both isomerides have the same molecular weight, and yield the same *o-nitrobenzamarone*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CHPh}\cdot\text{COPh})_2$ , m. p. 237—238°, when their alcoholic solutions are boiled with an equal molecular quantity of deoxybenzoin and a little sodium ethoxide; their alcoholic solutions, however, give different ultraviolet absorption spectra.

When an ethereal mixture of deoxybenzoin and *p*-nitrobenzaldehyde is treated with hydrogen chloride at 0°, and is kept for eleven days, a mixture is obtained, consisting chiefly of stout, yellow prisms of *iso-p-nitrobenzylidenedeoxybenzoin*, m. p. 164—165°, together with smaller amounts of elongated, yellow prisms of *allo-p-nitrobenzylidenedeoxybenzoin*, m. p. 148—149°, and white crystals of *chloro-p-nitrobenzyldeoxybenzoin*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}\cdot\text{CHPh}\cdot\text{COPh}$ , m. p. 157—158°, the three substances being separated by fractional crystallisation from alcohol; the last-mentioned compound is converted into a mixture of the other two by boiling 50% potassium hydroxide.

*p-Nitrobenzylidenedeoxybenzoin*, m. p. 133.5—135.5°, which crystallises in yellow prisms, is produced when a benzene solution (containing iodine) of the *iso*-compound is boiled for twelve hours in diffuse daylight. *p*-Nitrobenzylidenedeoxybenzoin and the *iso*- and *allo*-isomerides all have the same molecular weight, yield the same *dibromide*,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHBr}\cdot\text{CBrPh}\cdot\text{COPh}$ , decomposing at 156—157°, with bromine in carbon tetrachloride, produce the same *p-nitrobenzamarone*, m. p. 236—237°, and any one is converted into a mixture of the three by (i) exposing its benzene solution, containing iodine, to sunlight for four months, (ii) boiling the same solution for twelve hours in diffuse sunlight,

(iii) keeping its benzene solution, containing hydrogen chloride, for a week. All three give different absorption spectra in alcohol, and also their solutions in concentrated sulphuric acid, or in trichloroacetic acid, are colorimetrically different. A benzene or alcoholic solution of any one, even after being boiled, deposits, on cooling, only crystals of the ketone originally dissolved, even after inoculation with a crystal of either of the other two isomerides. When fused and cooled immediately, any one of the three isomerides resolidifies unchanged, but if kept in the molten condition for only five minutes a change occurs, and a mixture of the three ketones is formed.

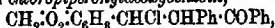
The action of hydrogen chloride on an ethereal solution of deoxybenzoin and *m*-nitrobenzaldehyde at 0° leads, after three days, to the formation of a white precipitate, consisting of two stereoisomeric (?) modifications of *α*-chloro-*m*-nitrobenzyldeoxybenzoin,



which are separated by crystallisation from benzene; one form crystallises in white needles, *m. p.* 181—182°, the other in stout, white crystals, *m. p.* 192—193°. When boiled with potassium hydroxide the latter yields *m*-nitrobenzylidenedeoxybenzoin, *m. p.* 85·5—86·5°, crystallising in white needles, whilst the former yields a mixture of *m*-nitrobenzylidenedeoxybenzoin and *iso-m*-nitrobenzylidenedeoxybenzoin, yellow prisms, *m. p.* 86·5—87·5°, the two being separated by crystallisation, first from ethyl acetate, and then from alcohol. *m*-Nitrobenzylidenedeoxybenzoin crystallises unchanged from boiling solutions; the *iso*-compound, however, is partly converted into *allo-m*-nitrobenzylidenedeoxybenzoin, *m. p.* 94·5—95·5°, which crystallises in white prisms. All three isomerides have the same molecular weight, form the same tribromide, decomposing at 159—161°, and the same *m*-nitrobenzamarone, *n. p.* 220—221°, and are mutually interconvertible by boiling their solutions in benzene, containing iodine, in diffuse daylight, by keeping their benzene solutions, containing hydrogen chloride, for a week, or by heating at 160°; by each method a mixture of the three isomerides is produced from any one. The *iso*- and the *allo*-isomerides show almost identical behaviour, giving the same absorption spectra in alcohol, different from that of *m*-nitrobenzylidenedeoxybenzoin, and solutions in concentrated sulphuric acid or trichloroacetic acid, which are colorimetrically the same. Solutions of the *iso*- or of the *allo*-isomeride in any solvent deposit mixtures of both, whilst *m*-nitrobenzylidenedeoxybenzoin alone separates from its solutions, even after inoculation with a crystal of either of the other two isomerides. All three melt and resolidify to the original substance if cooled at once, but when kept in a state of fusion for five minutes, *m*-nitrobenzylidenedeoxybenzoin changes to a mixture of the *iso*- and the *allo*-isomerides, *iso-m*-nitrobenzylidenedeoxybenzoin resolidifies unchanged, whilst the *allo*-isomeride partly changes to *m*-nitrobenzylidenedeoxybenzoin. When slowly heated, a mixture of equal parts of *m*-nitrobenzylidenedeoxybenzoin and the *iso*- or *allo*-isomeride fuses at a temperature below the *m. p.* of either constituent, whilst mixtures of the *iso*- and the *allo*-isomerides have the same *m. p.* as the *allo*-isomeride.

The action of hydrogen chloride on ethereal piperonal and deoxy-

benzoin at 0° leads, after twelve hours, to the production of a yellow mass, from which *chloropiperonyldeoxybenzoin*,



m. p. 167—168° (decomp.), is obtained in colourless crystals by crystallisation from benzene. The substance is converted into the *ethyl ether*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH(OEt):CHPh:COPh}$ , m. p. 114—115°, by boiling ethyl alcohol, into the corresponding *methyl ether*, m. p. 119—120°, by boiling methyl alcohol, and by boiling water into a mixture of *piperonylidenedeoxybenzoin*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH:CPh:COPh}$ , m. p. 128—129°, crystallising in white prisms, and *isopiperonylidenedeoxybenzoin*, m. p. 119—120°, crystallising in yellow prisms. The two isomerides give different absorption spectra. They can be recrystallised unchanged from solvents of low h. p., but either is converted into a mixture of the two by boiling its solution in benzene, containing iodine, in diffused daylight, or by the exposure of the same solution to sunlight at the ordinary temperature.

The nature of the isomerism described above is discussed at some length. There is no doubt that the *iso*- and the *allo*-isomerides resemble each other much more closely than the ketones with unprefix names. The last and the *iso*-isomerides are most probably *syn*- and *anti*-stereoisomerides. The *iso*- and the *allo*-isomerides undoubtedly differ from each other in solution and in the fused state; they are, therefore, true chemical isomerides, for the representation of which the ordinary formulæ do not suffice.

C. S.

**Ring Formation from the Ketonic Acids.** EDMOND E. BLAISE and A. KOEHLER (*Bull. Soc. chim.*, 1910, [iv], 7, 710—721).—It has been shown previously (Vorländer, *Abstr.*, 1897, i, 272; Blaise and Maire, *Abstr.*, 1908, i, 390) that the  $\delta$ -ketonic acids are condensed by sodium ethoxide to form derivatives of dihydroresorcinol.

The object of the present work was to determine whether this property persists in the  $\epsilon$ ,  $\zeta$ , and  $\eta$ -ketonic acids, in which the carbonyl group is farther removed from the carboxyl group in the molecule, and if so, the manner in which the ring-formation is effected.

The esters of the  $\epsilon$ -ketonic acids under the above conditions are transformed into 2-acylcyclopentanones. The fact that the product of the condensation of ethyl  $\alpha$ -acetyl- $n$ -valerate contains only one hydrogen atom replaceable by alkyl groups, shows that a heptamethylene derivative is not formed according to such a scheme as  $\text{CH}_2\text{:CH}_2\text{:CO:OEt} = \text{CH}_2\text{:CH}_2\text{:CO:CH}_2 + \text{EtOH}$ , and therefore that the reaction differs from that undergone by the  $\delta$ -ketonic acids. The 2-acylcyclopentanones, being  $\beta$  diketones, contain a hydrogen atom replaceable by sodium, the derivatives so formed being readily alkylated. Special precautions, however, are necessary in carrying out this alkylation, otherwise the closed carbon chain is ruptured by the action of the sodium ethoxide. The 2-acyl-2-alkylcyclopentanones are readily hydrolysed by alkalis, giving  $\delta$ -alkyl- $\epsilon$ -ketonic acids.

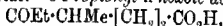
The esters of the  $\zeta$ -ketonic acids are similarly condensed by sodium

ethoxide, giving 2-alkylcyclohexanone, not octandione, derivatives, whilst the  $\eta$ -ketonic acids do not undergo ring-formation. The conclusion is drawn that compounds containing more than six carbon atoms in a closed chain cannot be produced by reactions of this kind.

2-Propionylcyclopentanone,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{COEt}) \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \rightarrow \text{CO}$  (Abstr., 1909, i,

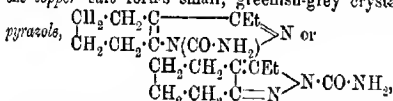
479), gives a violet coloration with ferric chloride; the copper salt forms grey leaflets; the magnesium salt, needles, m. p. 113—114° (decomp.), which contain 2H<sub>2</sub>O; the pyrazole crystallises in hexagonal prisms, m. p. 119°; in acetic acid it has a molecular weight corresponding with the formula C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>, but in benzene the molecular weight agrees with that of the azine, C<sub>16</sub>H<sub>24</sub>N<sub>4</sub>; the disemicarbazone forms a crystalline powder, m. p. 236°.

2-Propionyl-2-methylcyclopentanone is a colourless liquid, h. p. 94—96°/12 mm. It gives no coloration with ferric chloride. 2-Propionyl-2-ethylcyclopentanone has b. p. 107—108°/12 mm. It gives no coloration with ferric chloride.  $\delta$ -Propionyl-n-hexoic acid,



is a colourless liquid, h. p. 164°/10 mm.; the semicarbazone has m. p. 139·5°.  $\delta$ -Propionyl-n-heptoic acid, CH<sub>2</sub>Me·CH(COEt)·[CH<sub>2</sub>]<sub>5</sub>·CO<sub>2</sub>H, is a colourless liquid, b. p. 177°/11 mm.; the semicarbazone forms a white powder. m. p. 158—159°; the p-nitrophenylhydrazones forms canary-yellow crystals, m. p. 73° (rapid heating), 83—84° (slow heating); the ethyl ester has h. p. 136°/11 mm.

2-Propionylcyclohexanone (Abstr., 1909, i, 479) is a colourless liquid, having an agreeable odour resembling that of acetophenone; the copper salt forms small, greenish-grey crystals; the carbamido-



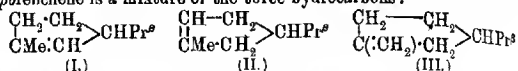
magnificent prisms, m. p. 126—127° (very rapid heating), 118° (slow heating), is formed under the conditions which give rise to the disemicarbazone in the case of the cyclopentanone. When treated with sodium ethoxide and an alkyl iodide, 2-propionylcyclohexanone gives an inseparable mixture of aliphatic esters.

E. H.

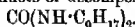
Constitution of Fenchone. III. LOUIS BOUVEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 736—740).—It has already been shown (Abstr., 1908, i, 193) that when diapofenchylcarbamide, CO(NH·C<sub>9</sub>H<sub>17</sub>)<sub>2</sub>, is heated with 40% sulphuric acid, an unsaturated hydrocarbon, apofenchene, C<sub>9</sub>H<sub>16</sub>, is formed. An attempt was made to characterise this hydrocarbon by preparing crystalline derivatives, but the additive compounds with hydrogen chloride and bromide and with nitrosyl chloride are liquids. From the product of the action of the nitrosochloride on piperidine, a trace of a substance, m. p. 175·5°, which is possibly the nitropiperidine, can be isolated. From the fact that, contrary to the original statement, the optical rotatory



power of the hydrocarbon is not constant, the authors conclude that apofenchene is a mixture of the three hydrocarbons:



which are the possible products of decomposition of the amide



The isomeride (II) is certainly present to a considerable extent, (I) is probably present, and the mixture perhaps contains a small quantity of the (III)<sub>a</sub> isomeride. The objection raised by Schimmel & Co. that a molecular transposition may have occurred during the reaction with sulphuric acid is controverted by the observation that the same hydrocarbon (b. p. 143°) is obtained by the action of nitrous acid on dihydrofencholenamide,  $\text{C}_{10}\text{H}_{17}\cdot\text{CO}\cdot\text{NH}_2$ .

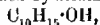
When an alcoholic solution of apofenchene is saturated with hydrogen chloride, the *hydrochloride*,  $\text{C}_{10}\text{H}_{17}\text{Cl}$ , is formed. It is a colourless, agreeably smelling liquid, b. p. 60°/8 mm.,  $D_4^{20}$  0.941,  $D_4^{25}$  0.927,  $n_D^{20}$  +1.24°. The *hydrobromide*, prepared similarly, is a very unstable substance, b. p. 83°/13 mm., losing hydrogen bromide and becoming black very readily. It is reduced by magnesium to apofenchene.

E. H.

**Sesquiterpene Alcohols.** H. KIMURA (*Ber. Deut. pharm. Ges.*, 1910, 20, 293—297).—The author has shown previously that liquid *isocryptomeriol*, by conversion into its xanthate and subsequent decomposition of the ester, is changed into solid *cryptomeriol* (this vol., i, 53). By similar treatment, *cedrol* is changed into its solid form, m. p. 86°, but *santalol* remains liquid, although its rotation is changed from  $-17^\circ 15'$  to  $-5^\circ$ . Also, the solid form of *cedrol* is obtained when the alcohol or its potassium derivative is distilled with superheated steam and the distillate is kept for several weeks.

C. S.

**Oil of Savin.** FRITZ ELZE (*Chem. Zeit.*, 1910, 34, 767—768). A product can be isolated from oil of savin which is easily soluble in dilute alcohol, and has a more intense odour than the original oil. It has  $D_{15}^{20}$  0.960, and  $n_{106}^{20}$  +68°. On saponification with alcoholic potassium hydroxide and fractional distillation under diminished pressure of the product obtained by steam distillation, *sabinol*,



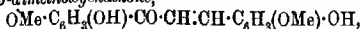
was obtained ( $D_{15}^{20}$  0.950 and  $n_{106}^{20}$  +6°). The acetate prepared from this *sabinol* had  $D_{15}^{20}$  0.972,  $n_{106}^{20}$  +79°, and b. p. 81—82°/3 mm. The original oil thus consisted mainly of *sabinol* acetate, about 83%.

The following products were also isolated in the fractional distillation: *n*-decaldehyde, *geraniol*, and *dihydrocumyl* alcohol.

T. S. P.

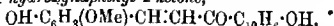
**Curcupin.** J. MŁOBYDZKA, STANISLAUS VON KOSTANECKI, and VIKTOR LAMPE (*Ber.*, 1910, 43, 2163—2170).—Various hydroxy-chalkones have been synthesised in order to compare them with

curcumin. They resemble this compound, but do not dye unmordanted cotton. Vanillin condenses but slowly with pæonol, yielding 2':4-di-hydroxy-4':3'-dimethoxychalkone,



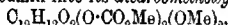
which crystallises from alcohol in yellow needles, m. p. 142—143°. The diacetyl derivative,  $\text{C}_{21}\text{H}_{20}\text{O}_7$ , forms yellow prisms, m. p. 155°.

2':4'-Dihydroxy-5':3'-dimethoxychalkone,  $\text{C}_{17}\text{H}_{16}\text{O}_5$ , prepared from vanillin and quinacetophenone monomethyl ether, crystallises from alcohol in orange-coloured plates, m. p. 122—123°. 4-Hydroxy-3-methoxystyryl 1-hydroxynaphthyl 2-ketone,

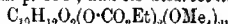


prepared from vanillin, 2-aceto-1-naphthol, alcohol, and sodium hydroxide solution, crystallises from alcohol in red needles, m. p. 190—191°. Its solution in concentrated sulphuric acid has a reddish-yellow colour. The diacetyl derivative,  $\text{C}_{24}\text{H}_{20}\text{O}_8$ , crystallises in yellow needles, m. p. 162—164°.

The presence of the CO·C:C group in curcumin is proved by the fact that ferulic acid (4-hydroxy-3-methoxycinnamic acid) is formed when curcumin is boiled with 20% potassium hydroxide solution. The formula  $[\text{OH} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{CH} \cdot \text{CO}]_2\text{CH}_2$  is suggested as accounting for all the properties of curcumin. The formula  $\text{C}_{21}\text{H}_{20}\text{O}_6$  (compare Latham and Loring Jackson, Abstr., 1908, i, 670) has been confirmed by conversion of curcumin into its dicarbomethoxy-derivative,

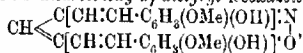


deep yellow prisms, m. p. 150°, and its dicarbomethoxy-derivative,



yellow plates, m. p. 149—150°.

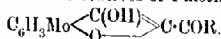
Hydroxylamine reacts with the dicarbomethoxy-derivative, yielding 3:3'-dimethoxy-4:4'-dicarbomethoxy- $\alpha$ -distyryl-isooxazole,



as colourless plates, m. p. 139—140°. The same compound can also be obtained by the action of ethyl chloroformate on Ciamician and Silber's oxime-anhydride,  $\text{C}_{21}\text{H}_{19}\text{O}_5\text{N}$  (Abstr., 1897, i, 229).

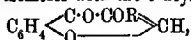
J. J. S.

C- and O-Acyl Derivatives of Coumaranones or 2-Hydroxy-coumarones. KARL AUWERS (*Ber.*, 1910, 43, 2192—2202).—By the interaction of organic bases and esters of 3-chloroacetyl-*p*-cresol, compounds of the type  $\text{C}_6\text{H}_3\text{Me}(\text{OH}) \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NPh} \cdot \text{COR}$  are formed, together with other substances containing nitrogen (compare Auwers, Abstr., 1909, i, 222). In presence of weak alkalis, the reaction takes quite another course, nitrogen-free substances being the sole product. These were at first taken to be flavonols or chromonols, but this idea was disproved by comparison with 2-methylflavonol, and the new compounds shown to be keto-derivatives of 4-methylcoumarone,



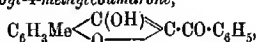
They form salts, ethers, and esters, and where  $\text{R} = \text{CH}_3$  behave as ketones, although when R is an aromatic radicle, steric influences

prevent the formation of ketonic derivatives. Of the three possible desmotropic structural formulae for the new compounds, the above is shown to be the most probable, and they are 1- or *C*-acyl-2-hydroxy-coumarone derivatives, isomeric with the *O*-acyl compounds,



formed by acylation of coumaranones. The esters of the new ketones represent mixed *O,C*-diacyl derivatives. 3-Chloroacetyl-*p*-cresol forms an *anisoyl* derivative crystallising in short, lustrous, pointed prisms, *m. p.* 121.5°.

2-Hydroxy-1-benzoyl-4-methylcoumarone,



produced by boiling a mixture of 3-chloroacetyl-*p*-cresol, potassium carbonate and benzene, has *m. p.* 112°, and crystallises from alcohol in pale yellow, silky needles, which change readily into short, lustrous, four-sided plates. The compound forms a sparingly soluble sodium salt, dissolves in sodium hydroxide with an intense yellow coloration, and in sulphuric acid gives a yellow solution with a green fluorescence. It does not react with ketone reagents. The acetate crystallises in stellar aggregates of short, glistening needles, *m. p.* 81—82°. The benzoate forms colourless, glistening prisms, *m. p.* 137°.

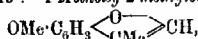
2-Hydroxy-1-anisoyl-4-methylcoumarone forms long, slender, sulphur-yellow, lustrous needles, *m. p.* 145.5°.

2-Hydroxy-1-acetyl-4-methylcoumarone,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{C}(\text{OH}) \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C} \cdot \text{COMe}$ ,

crystallises in long, glistening needles, *m. p.* 86—87°; it is coloured orange-yellow by sulphuric acid. Alkaline hydrogen peroxide oxidises it to *p*-homosalicylic acid. The benzoate separates in colourless, matted needles, *m. p.* 128—129°; the semicarbazone forms colourless or slightly yellow needles, which become yellow at 195°, *m. p.* 202° (decomp.). The phenylhydrazone forms long, yellow needles, *m. p.* 138°.

2-Benzoyloxy-4-methylcoumarone,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \text{C}(\text{OBz}) \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{CH}_2$ , prepared from methylcoumaranone, benzoyl chloride, and sodium hydroxide, forms yellow needles, *m. p.* 64—65°. E. F. A.

The Coumarone Group. A. von GRAFFENRIED and STANISLAUS VON KOSTANECKI (*Ber.*, 1910, 43, 2155—2157. Compare *Abstr.*, 1908, i, 442; 1909, i, 319).—Ethyl bromoacetate reacts with quinaeto-phenone monomethyl ether in the presence of sodium ethoxide, yielding ethyl 2-acetyl-4-methoxyphenoxyacetate,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Ac} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , and this when hydrolysed with alcoholic potassium hydroxide yields the corresponding acid,  $\text{C}_{11}\text{H}_{12}\text{O}_6$ , which crystallises in broad needles, *m. p.* 144—145°. 4-Methoxy-2-methylcoumarone,

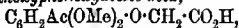


obtained by heating the acid with acetic anhydride and sodium acetate, is a colourless oil, *b. p.* 245°/706 mm., with an aromatic odour. It

solution in concentrated sulphuric acid has an orange colour with a green fluorescence.

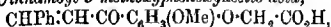
*2-Acetyl-4-ethoxyphenoxyacetic acid*,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{Ac} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , crystallises in needles, m. p. 138—139°, and *4-ethoxy-2-methylcoumarone*,  $\text{C}_{11}\text{H}_{12}\text{O}_3$ , is a colourless oil, b. p. 257°/718 mm.

*2-Acetyl-5:6-dimethoxyphenoxyacetic acid*,



obtained from gallacetophenone methyl ether, has m. p. 104—106°, and *5:6-dimethoxy-2-methylcoumarone*,  $\text{C}_8\text{H}_8(\text{OMe})_2 \cdot \text{O} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{OMe})_2$ , has b. p. 278—279°/702 mm. J. J. S.

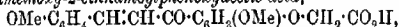
**Derivatives of 2-Styrylcoumarone.** J. ABELIN and STANISLAUS VON KOSTANECKI (*Ber.*, 1910, 43, 2157—2162. Compare preceding abstract).—*2-Cinnamoyl-5-methoxyphenoxyacetic acid*,



obtained by condensing benzaldehyde and 2-acetyl-5-methoxyphenoxyacetic acid (*Abstr.*, 1909, i, 319) in the presence of alkali, crystallises from alcohol in colourless plates, m. p. 166—167°. The *ethyl ester*,  $\text{C}_{20}\text{H}_{20}\text{O}_5$ , forms colourless needles, m. p. 89°. *5-Methoxy-2-styrylcoumarone*,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \cdot \text{O} \cdot \text{CH} \cdot \text{CH} \cdot \text{C}(\text{CH})_2$ , is formed when the acid is

heated with acetic anhydride and sodium acetate. It crystallises from alcohol in colourless needles, m. p. 77—78°, and gives a bright red colour when moistened with concentrated sulphuric acid.

*5:2-Dimethoxy-2-cinnamoylphenoxyacetic acid*,

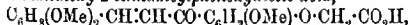


obtained from o-methoxybenzaldehyde and 2-acetyl-5-methoxyphenoxyacetic acid, crystallises from alcohol in yellow prisms or colourless needles, m. p. 128°. The *ethyl ester*,  $\text{C}_{21}\text{H}_{22}\text{O}_6$ , has m. p. 111°, and *5:2-dimethoxy-2-styrylcoumarone*,  $\text{C}_{18}\text{H}_{16}\text{O}_5$ , crystallises from alcohol in rhombic plates, m. p. 75°.

*5:3'-Dimethoxy-2-cinnamoylphenoxyacetic acid*,  $\text{C}_{19}\text{H}_{18}\text{O}_6$ , forms colourless needles, m. p. 142—143°; its *ethyl ester*,  $\text{C}_{21}\text{H}_{22}\text{O}_6$ , has m. p. 96°, and *5:3'-dimethoxy-2-styrylcoumarone*,  $\text{C}_{18}\text{H}_{16}\text{O}_5$ , crystallises in needles or plates, m. p. 120—121°.

*5:4'-Dimethoxy-2-cinnamoylphenoxyacetic acid* has m. p. 162—163°; its *ethyl ester* has m. p. 117°, and *5:4'-dimethoxy-2-styrylcoumarone* has m. p. 126°.

*5:3':4'-Trimethoxy-2-cinnamoylphenoxyacetic acid*,



obtained from veratraldehyde, crystallises in plates, m. p. 175°, and gives a dark red coloration with concentrated sulphuric acid. The *ethyl ester*,  $\text{C}_{28}\text{H}_{28}\text{O}_7$ , crystallises in yellow plates, m. p. 129—130°, and *5:3':4'-trimethoxy-2-styrylcoumarone*,  $\text{C}_{19}\text{H}_{18}\text{O}_6$ , forms colourless needles, m. p. 106°. Its solution in sulphuric acid has a magenta-red colour. All attempts to transform this compound into a trimethoxy-dihydroisobranan by ring formation proved fruitless. J. J. S.

**Formation of Pyrene from Thebaine.** MARTIN FREUND (*Ber.* 1910, 43, 2128—2130).—The formation of pyrene from thebaine is

confirmed (compare Freund, Abstr., 1897, i, 496). Pyrene is formed, not merely when the alkaloid is distilled with zinc dust, but also when it is reduced with hydriodic acid and red phosphorus. The latter fact invalidates to a large extent Pschorr's criticism (this vol., i, 423) of the author's formula for thebaine.

J. J. S.

**New Preparation of 1-Alkylpyrrolidines.** KARL LÖFFLER (Ber., 1910, 43, 2035—2048. Compare Abstr., 1909, i, 830).—The method previously described, bromination of an amine at the nitrogen atom and elimination of hydrogen bromide by means of concentrated sulphuric acid, has been extended to the preparation of 1-methyl-2-propylpyrrolidine and of 1:2-dimethyl-, 1-methyl-2-ethyl-, and 1:3-dimethyl-pyrrolidines. Attempts were made to extend it to such amines as would yield piperidine derivatives or four-membered rings, but without result.

[With CURT FREYTAG.]—*β*-Methylamino-*n*-heptane, prepared from methylamine and dipropyl ketone, and subsequent reduction, has b. p. 148°,  $D_{15}^{20}$  0.77; the *aurichloride* separates in well formed yellow needles, m. p. 99°; the *platinichloride* forms orange plates, m. p. 193—195°; the *picrate* separates in long, light yellow needles, m. p. 96°; the *hydrochloride* is very hygroscopic.

1-Methyl-2-propylpyrrolidine is a colourless liquid, h. p. 146—147°/761 mm.,  $D_{15}^{20}$  0.815. The *picrate* forms yellow needles, m. p. 124°; the *platinichloride* forms orange plates, m. p. 145—146°; the *aurichloride* also forms yellow plates, m. p. 76°. The *ethochloride* gives a *platinichloride*, orange plates, m. p. 226—227°, and an easily decomposed yellow *aurichloride*.

Methyl-*n*-amylamine has b. p. 116—118°,  $D_{15}^{20}$  0.738; the *picrate* forms yellow needles, m. p. 119—120°; the *hydrochloride* forms needles, m. p. 181—182°; the *platinichloride* separates in yellow needles, m. p. 171—173°; the *aurichloride* is a yellow oil. It could be converted into 1-methylpiperidine in the manner described.

*β*-Methylamino-*n*-butane has b. p. 78—79°,  $D_{15}^{20}$  0.74; the *aurichloride* forms yellow needles, m. p. 58°; the *platinichloride* forms dark orange crystals, m. p. 151°; the *picrate* forms light yellow needles, m. p. 78°. No ring compound was formed on heating the brominated amine with concentrated sulphuric acid.

[With MARIAN LUKOWSKY.]—Methylisoamylamine (compare Stoermer and Lepel, Abstr., 1896, i, 663) has b. p. 108—110°,  $D_{15}^{20}$  0.7428; *hydrochloride*, m. p. 181°; *platinichloride*, m. p. 208—209°; *aurichloride*, needles, m. p. 68—70°; *picrate*, m. p. 112°.

1:3-Dimethylpyrrolidine has an odour of piperidine, b. p. 96—97°,  $D_{15}^{20}$  0.792. The *picrate* shows dimorphism, separating first in long crystals, m. p. 181—182°, which change when kept in alcoholic solution into granular crystals, m. p. 110—115°: these on recrystallisation give the less fusible variety. The *hydrochloride* is hygroscopic; the *platinichloride* forms garnet-red, granular crystals, m. p. 58—59°; the *aurichloride* crystallises in characteristic, feathery, interlaced needles, m. p. 137°; the *mercurichloride* has m. p. 200—201°. The *ethiodide* is a hygroscopic, colourless powder; of the *ethochloride* the

*platinichloride* has m. p. 243—244° (decomp.); the *aurichloride*, m. p. 200—201°.

[With WALDEMAR BOBILOFF.]— $\beta$ -Methylamino-n-pentane, from methylamine and methyl propyl ketone, is a colourless, mobile liquid, b. p. 103—104°/754 mm.,  $D^{20}_D$  0.747. The *platinichloride* forms yellowish-red needles, m. p. 137.5°; the *aurichloride* is an oil; the *picrate* forms broad needles, m. p. 77—78°. It is readily converted into 1:2-dimethylpyrrolidine, of which the *picrate* has m. p. 233.5°, and the *platinichloride* of the *ethochloride*, m. p. 249° (decomp.).

$\gamma$ -Methylaminoheptane is a transparent, mobile, strongly basic liquid, b. p. 126—128°/754 mm.,  $D^{20}_D$  0.761. The *platinichloride* is a flesh-coloured powder, m. p. 162—163°; *aurichloride* and *picrate* are oily.

1-Methyl-2-ethylpyrrolidine is a transparent, strongly basic liquid, b. p. 122—123°/763 mm.,  $D^{15}_D$  0.8124. The *platinichloride* forms intergrown needles, m. p. 210—211°; the *aurichloride*, well formed needles, m. p. 112°; the *picrate*, golden-yellow plates, m. p. 170°. The *platinichloride* of the *ethochloride* begins to decompose at 243°, m. p. about 250°.

E. F. A.

Synthesis of  $\delta$ -Methylconidine and of Derivatives of 2-Methyl-6-ethylolpiperidine. KARL LÖFFLER and HANS REMMLER (*Ber.*, 1910, 43, 2048—2059. Compare Königs and Hapfe, *Abstr.*, 1903, i, 850. Löffler and Thiel, *Abstr.*, 1909, i, 182).—By the condensation of 2:6-lutidine with formaldehyde, 2-methyl-6-ethylolpyridine, b. p. 126—128°/16 mm., and 2:6-diethylolpyridine, b. p. 185—195°/16 mm., are obtained. The former, when reduced by means of sodium and alcohol, gives 2-methyl-6-ethylolpiperidine; the crude base has b. p. 226—232°, and is a mixture of stereoisomerides. One form separates from ether in glistening, rhombic crystals, m. p. 95—96°; the *aurichloride* has m. p. 104°; the *platinichloride* forms broad crystals, m. p. 180—181°; the *picrate* has m. p. 127°. The stereoisomeride was obtained as a viscid syrup, of which the *picrate* separates in long needles, m. p. 187°; the *aurichloride* has m. p. 99—100°; the *platinichloride* forms short, granular crystals, m. p. 198—199°.

2-Methyl-6-ethylolpiperidine has very little poisonous action. Attempts to resolve it into optically active modifications by means of tartaric acid were not successful.

When heated under pressure with fuming hydrochloric acid and red phosphorus, a *hydriodide iodide* is formed, crystallising in colourless, short needles, m. p. 192—193°. On warming with sodium hydroxide, this is converted into  $\delta$ -methylconidine,  $\begin{array}{c} \text{CH}_2\text{CH}_2-\text{CH}\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CHMe}\cdot\text{N}-\text{CH}_2 \end{array}$ , a colour-

less, mobile liquid with an unpleasant concine-like odour, b. p. 156°,  $D^{20}_D$  0.8931. The *picrate* forms large, pointed needles, m. p. 237°; the *aurichloride* is amorphous, m. p. 191—192°; the *platinichloride* forms broad needles, m. p. 198°. The *ethiodide* has m. p. 202° (decomp.); the *platinichloride* of the *ethochloride* has m. p. 210.5°.

By the action of phosphorus pentachloride on 2-methyl-6-ethylolpiperidine, 2-methyl-6-vinylpiperidine is obtained; the colourless, mobile liquid has b. p. 150°,  $D^{20}_D$  0.8381. The *hydrochloride* forms colourless, slender needles, m. p. 242.5—243°; after crystallisation of

the salt, the mother liquors become an intense red colour after a time. The *picrate* crystallises in tabular plates, m. p. 123°; the *platinichloride* in long needles, m. p. 176°.

Chromic acid oxidises 2-methyl-6-ethylpiperidine to 2-methylpiperidyl-6-acetic acid, crystallising in colourless, matted needles, m. p. 219–220°. The *hydrochloride* crystallises similarly, m. p. 192–206° (decomp.); the *aurichloride* forms needles, m. p. 129–131°; the *platinichloride*, granular crystals, m. p. 207°.

2:6-Diethylpiperidine is obtained by reducing diethylpyridine as a viscid. oil, h. p. 168–169°/18 mm.; it crystallises in reniform aggregates. The *picrate* has m. p. 136°.

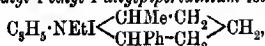
On acetylating 2-methyl-6-ethylpiperidine with warm acetic anhydride, a *diacetate* is formed, a colourless, viscid liquid, b. p. 190–200°/25 mm.,  $D_4^{20}$  1.703; the two acetyl groups are probably attached to nitrogen and in the side-chain respectively; both are hydrolysed by 1% alcoholic hydrochloric acid. Acetylation in the cold with acetic anhydride gives the *monoacetate*, b. p. 105–110°/25 mm., a mobile, colourless, strongly alkaline liquid, which forms stable salts, and therefore is acetylated in the side-chain. The *aurichloride* crystallises in reniform aggregates, m. p. 118°. It was not found possible to cause this acetyl group to wander to the nitrogen atom. E. F. A.

**Stereochemistry of Quinquevalent Nitrogen.** MAX SCHOLTZ (*Ber.*, 1910, 43, 2121–2126. Compare *Abstr.*, 1904, i, 1044; 1905, i, 296, 473; 1908, i, 678; Scholtz and Wassermann, 1907, i, 340; Voss and Gadamer, *this vol.*, i, 415).—Two stereoisomeric quaternary ammonium salts are formed by the union of allyl iodide with *dl*-6-phenyl-2-methyl-1-ethylpiperidine, and from these quaternary salts well defined, crystalline isomeric *platinichlorides* have been prepared.

Stereoisomeric quinquevalent nitrogen compounds of the type *Na<sub>3</sub>bcd* have been prepared by condensing *o*-xylylene bromide with 2-phenyl-6-methylpiperidine (compare *Abstr.*, 1898, i, 565). These compounds differ from the stereoisomerides described by Aschan (*Abstr.*, 1904, i, 350), as they contain only one nitrogen atom.

6-Phenyl-2-methyl-1-propylpiperidine,  $\text{NPr} \begin{smallmatrix} \text{CHMe-CH}_2 \\ \text{CHPh-CH}_2 \end{smallmatrix} > \text{CH}_2$ , prepared by boiling 2-phenyl-6-methylpiperidine (Scholtz and Müller, *Abstr.*, 1901, i, 41) with *n*-propyl iodide and potassium hydroxide, is a colourless liquid with a basic odour, has h. p. 264–265° (corr.) and  $D_4^{20}$  0.9101. It combines with benzyl iodide, yielding an oily 2-phenylbenzyl-6-methyl-*n*-propylpiperidinium iodide,  $\text{C}_{22}\text{H}_{33}\text{NI}$ , from which only a small amount of colourless crystals were isolated.

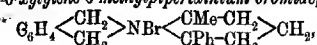
*dl*-2-Phenyl-6-methyl-1-ethyl-1-allylpiperidinium iodide,



exists in an oily ( $\alpha$ ) and a crystalline ( $\beta$ ) form. The latter forms colourless prisms, m. p. 198°. The  $\alpha$ -*platinichloride*,  $(\text{C}_{17}\text{H}_{25}\text{N})_2\text{PtCl}_6$ , crystallises in orange-red needles, m. p. 211° (decomp.); the isomeric compound forms similar needles, m. p. 223°. The two *hydrochlorides* are deliquescent solids. The  $\alpha$ -*aurichloride* is an oil which solidifies to

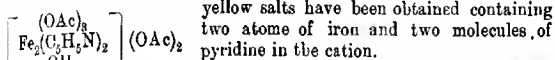
a resinous mass, and the  $\beta$ -aurichloride,  $C_{17}H_{26}NAuCl_4$ , crystallises in golden, yellow needles, m. p.  $136^\circ$ .

$\alpha$ -2-Phenyl-1-o-xylylene-6-methylpiperidinium bromide,



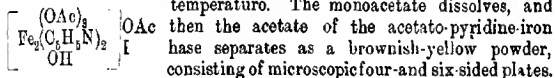
crystallises from water in rhombic prisms, m. p.  $226^\circ$ . The  $\beta$ -compound separates from solvents as an oil which solidifies when rubbed; it has m. p.  $228^\circ$ . The  $\alpha$ -platinichloride has m. p.  $238^\circ$ , and the  $\beta$ -compound, m. p.  $259^\circ$ . The aurichlorides are oily. J. J. S.

An Acetato-Pyridine-Iron Base and a Very Basic Pyridine-containing Ferric Acetate. RUDOLF WEINLAND and E. GUSSMANN (*Ber.*, 1910, 43, 2144—2149).—By the action of pyridine on the acetate of the hexa-acetato-triferri-base (Abstr., 1909, i, 872), brownish-yellow salts have been obtained containing



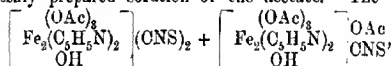
two atoms of iron and two molecules of pyridine in the cation.

The acetate (annexed formula) is obtained by leaving 20 grams of the monoacetate of the hexa-acetato-triferri-base in contact with 50—60 gramme of anhydrous pyridine at the ordinary temperature. The monoacetate dissolves, and

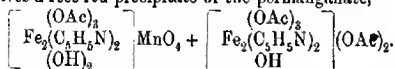


then the acetate of the acetato-pyridine-iron base separates as a brownish-yellow powder, consisting of microscopic four- and six-sided plates.

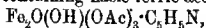
The iodide (annexed formula) separates as a brownish-yellow precipitate when a saturated solution of potassium iodide is added to the freshly prepared solution of the acetate. The thiocyanate,



separates as a chocolate-brown powder on the addition of a saturated solution of sodium thiocyanate to the aqueous solution of the acetate. Under the same conditions, a saturated solution of potassium permanganate gives a rose-red precipitate of the permanganate,



When 5 gramme of pyridine are added to 30 c.c. of a 12% solution of the monoacetate of the hexa-acetato-triferri-base (*loc. cit.*) and the solution maintained at a temperature not exceeding  $15^\circ$ , dark red crystals of a pyridine-containing basic ferric acetate,

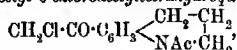


separate after some hours. A copper-red acetate of a pyridine-containing acetato-iron base has also been obtained, but requires further investigation. T. S. P.

Derivatives of Tetrahydroquinoline. III. Ketones and Acids of Tetrahydroquinoline and of Tetrahydro-*o*- and *p*-toluquinoline. FRANZ KUNCKEL (*Ber. Deut. pharm. Ges.*, 1910, 20, 277—293).—The interaction of 1-acetyltetrahydroquinoline, chloroacetyl chloride, and aluminium chloride in carbon disulphide leads to



the formation of 1-acetyl-6-chloroacetyltetrahydroquinoline,

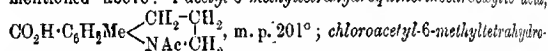


m. p. 137°, which is converted into 1-acetyltetrahydroquinoline-8-carboxylic acid, m. p. 187°, by hot alkaline hydrogen peroxide, into a trinitrotetrahydroquinoline, m. p. 152°, by concentrated nitric acid, and into 1-acetyl-6-chlorobromoacetyltetrahydroquinoline, m. p. 179°, by bromination in glacial acetic acid; the last-mentioned compound is oxidised to the preceding acid, m. p. 187°, by alkaline hydrogen peroxide. The hydrolysis of 1-acetyl-6-chloroacetyltetrahydroquinoline by 20% hydrochloric acid on the water-bath yields 6-chloroacetyltetrahydroquinoline, m. p. 123—124°, an alcoholic solution of which at 5—10° is converted by nitrous fumes into the nitrosoamine, m. p. 140°.

1-Acetyl-6-bromoacetyltetrahydroquinoline has m. p. 134°.

1-Acetyl-6-methyltetrahydroquinoline is not only attacked more readily than 1-acetyltetrahydroquinoline by chloroacetyl chloride or bromoacetyl bromide, but reacts even with acetyl bromide itself, which is not the case with 1-acetyltetrahydroquinoline. 1,4-Di-

acetyl-6-methyltetrahydroquinoline has m. p. 160°. 1-Acetyl-1-chloroacetyl-6-methyltetrahydroquinoline, m. p. 132°, and 1-acetyl-4-bromoacetyl-6-methyltetrahydroquinoline, m. p. 128°, are obtained in the same manner as 1-acetyl-6-chloroacetyltetrahydroquinoline, and are converted into the following substances by reactions similar to those mentioned above: 1-acetyl-6-methyltetrahydroquinolinecarboxylic acid,



quinoline, m. p. 122°, (hydrochloride, m. p. 218°); 1-acetyl-1-chlorobromoacetyl-6-methyltetrahydroquinoline, m. p. 143°; when heated with concentrated nitric acid, 1-acetyl-1-chloroacetyl-6-methyltetrahydroquinoline yields a substance, m. p. 259° (decomp.), which is probably a nitropiperidinecarboxylic acid.

The following derivatives of 1-acetyl-8-methyltetrahydroquinoline are obtained by similar processes: 1-acetyl-1-chloroacetyl-8-methyltetrahydroquinoline, m. p. 120°; 1-acetyl-1-bromoacetyl-8-methyltetrahydroquinoline, m. p. 125—126°; 1-acetyl-8-methyltetrahydroquinolinecarboxylic acid, m. p. 108°; the acetyl group cannot be introduced into 1-acetyl-8-methyltetrahydroquinoline. C. S.

**Method of Preparation of  $\alpha$ -Benzoylated Phenylhydrazines.** GEORG LOCKEMANN (*Ber.*, 1910, 43, 2223—2230).—Lockemann and Liesche (*Abstr.*, 1905, i, 570) have shown that by the action of benzoyl chloride on phenylethylidenehydrazine in presence of dry pyridine,  $\alpha$ -benzoyl- $\alpha$ -phenyl- $\beta$ -ethylidenehydrazine is obtained. It is absolutely necessary to exclude all traces of moisture, otherwise the ethylidene group is eliminated, and di- and tri-benzoyl derivatives are obtained. Using dry pyridine, it is possible to benzoylate also with *m*- and *p*-nitro- and *p*-chloro-benzoyl chloride, but not with the *o*-nitro-derivative.

The action of excess of mineral acids in cold solution eliminates the ethylidene group from these hydrazines as aldehyde, and the salts of  $\alpha$ -benzoylhydrazones are obtained.

[With TH. LOBENSTEIN, H. ENDE, and F. HEROLD].—*a*-Benzoyl-*a*-phenyl- $\beta$ -ethylidenehydrazine forms colourless, rectangular plates, m. p. 90–91°. It gives *a*-benzoylphenylhydrazine (Michaelis and Schmidt, Abstr., 1887, 820), m. p. 70°; the hydrochloride forms colourless needles, m. p. 202°.

*a*-p-Nitrobenzoyl-*a*-phenyl- $\beta$ -ethylidenehydrazine crystallises in light yellow prisms with pointed ends, m. p. 116–117°; alcoholic hydrogen chloride converts it into the hydrochloride of *a*-p-nitrobenzoyl-*a*-phenylhydrazine, also crystallising in light yellow needles, which sinter at 183°, m. p. 195–196° (decomp.). The free base forms light yellow, lustrous crystals, m. p. 141–142°; the acetyl derivative, *a*-p-nitrobenzoyl- $\beta$ -acetyl-*a*-phenylhydrazine, separates in light yellow crystals, m. p. 184–185°.

*a*-m-Nitrobenzoyl-*a*-phenyl- $\beta$ -ethylidenehydrazine forms yellowish-white plates, m. p. 124–125°; *a*-m-nitrobenzoylphenylhydrazine forms yellowish-white, six-edged plates, m. p. 123–124°; the hydrochloride crystallises in yellowish-white, pointed needles, m. p. 176–177° (decomp.).

*a*-p-Chlorobenzoyl-*a*-phenyl- $\beta$ -ethylidenehydrazine was obtained in yellow, short, rhombic crystals and in colourless, reniform prisms, both m. p. 90–91°. On keeping, the colourless prisms slowly change to the yellow, stable form; on crystallisation, the labile, colourless forms are the first to separate.

When moisture is present, *p*-chlorobenzoic anhydride is obtained, instead of the foregoing; it crystallises in lustrous, long, colourless prisms and needles, m. p. 193–194°.

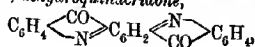
*a*-p-Chlorobenzoyl-*a*-phenylhydrazine forms colourless rhombs with pointed angles, m. p. 128–129°. The hydrochloride crystallises in colourless, lustrous needles, m. p. 192–193°.

E. F. A.

Syntheses of Polypeptides. Derivatives of Pyrrolidone-carboxylic Acid. EMIL ABERHALDEN and AKIKAZU SUWA (*Ber.*, 1910, 43, 2151–2155).—Pyrrolidonecarboxylic chloride can be obtained by the action of thionyl chloride or of a mixture of acetyl chloride and phosphorus pentachloride on the acid, and condenses with ethyl glycine, yielding ethyl pyrrolidonylglycine,  $C_9H_{14}O_4N_2$ , which crystallises from alcohol in colourless needles, m. p. 134° (corr.). When hydrolysed with concentrated hydrochloric acid, the ester yields the hydrochlorides of glutamic acid and of glycine ester.

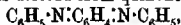
Pyrrolidonylglycine,  $\begin{array}{c} CH_2CH_2 \\ | \\ CO-NH \end{array} > CH \cdot CO \cdot NH \cdot CH_2 \cdot CO_2H$ , can be prepared by hydrolysing the ester by shaking with *N*-sodium hydroxide solution; it crystallises in slender needles, m. p. 168° (corr.), and yields a hygroscopic copper salt,  $(C_7H_9O_4N_2)_2Cu \cdot 2H_2O$ . J. J. S.

Quinone Diimines of the Acridone Series. LUDWIG KALB (*Ber.*, 1910, 43, 2209–2214).—By the oxidation of the yellow quinaclidone discovered by Ullmann and Maag (Abstr., 1906, i, 459) with lead oxide in indifferent solvents in presence of acetic acid, a new quinonedi-imine, dehydroquinaclidone,



is obtained, which has a remarkable greenish dark-blue colour in solution.

It may be regarded as derived from quinonedianil,



which is orange-red; the colour is deepened to blue by the presence of the two acridone rings. The corresponding compound with but one

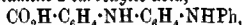
acridone ring, *dehydro-2-anilinoacridone*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_5\cdot\text{N}\cdot\text{C}_6\text{H}_5$ , obtained by the oxidation of 2-anilinoacridone with lead oxide, is dark red.

Dehydroquinacridone, like dehydroindigotin, has a strong oxidising action, and liberates other quinones and quinonedi-imines from their hydro-compounds, and oxidises indigotin to dehydroindigotin. The oxidising power may be determined by titration with ethereal quinol solution, the colour changing from blue through green to yellow. It liberates chlorine from cold fuming hydrochloric acid.

2-Anilinodehydroacridone does not possess such marked oxidising powers, but oxidises quinol to quinone.

*Dehydroquinacridone* crystallises in bluish-black, hexagonal plates. It dissolves in sulphuric acid with decomposition, showing a brownish-yellow coloration and green fluorescence.

4'-Anilinodephenylamine-2-carboxylic acid,



prepared by the condensation of *p*-aminodiphenylamine with *o*-chlorobenzonic acid, crystallises in pale yellow plates, m. p. 199° (green coloration and decomp.). The colourless solution in sulphuric acid gives a cherry-red coloration with traces of nitric acid.

2-Anilinoacridone, prepared by warming the above compound with sulphuric acid at 85°, forms yellow, crystalline crusts, m. p. 303—305°. The solutions are yellow and fluoresce green; that in sulphuric acid is faintly red, and has an intense blue fluorescence. The *hydrochloride* forms long, red, prismatic plates, which change to yellow at 250°.

2-Anilinodehydroacridone forms long, pointed, blackish-brown plates, which partly melt at 145°, decomp. 280°. It dissolves and decomposes in sulphuric acid with a reddish-brown colour and blue fluorescence.

E. F. A.

**Derivatives of Iminazole [Glyoxaline] and Histidine containing Iodine.** HERMANN PAULY (*Ber.*, 1910, 43, 2243—2261. Compare Pauly and Gundermann, *Abstr.*, 1909, i, 71).—It has been shown for triiodoglyoxaline that all three carbon atoms in the ring can fix iodine, and the preparation of a hydrochloride showed that no iodine was attached to nitrogen. This constitution is now confirmed by the preparation of a *silver* compound and of an *N-ethyl* derivative, and, further, by the continued action of iodine and alkali, leading to the formation of

1:2:4:5-tetraiodoglyoxaline,  $\begin{smallmatrix} \text{I} & \text{NI} \\ | & \diagup \\ \text{Cl}-\text{N} & \text{Cl} \end{smallmatrix}$ . In addition, 4:5-di-iodo-

2-methylglyoxaline, from 2-methylglyoxaline, 1:4:5-tri-iodo-2-methylglyoxaline, and 1-iodo-2:4:5-trimethylglyoxaline,  $\begin{smallmatrix} \text{CMe} & \text{NI} \\ | & \diagup \\ \text{CMe}-\text{N} & \text{CMe} \end{smallmatrix}$ , have

been prepared so as to allow of a comparison between glyoxalines containing iodine attached to C or N.

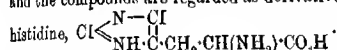
The C-compounds are more soluble, more definitely crystalline, they form metallic and acid salts, and melt without much loss of iodine.

The N-compounds are sparingly soluble in indifferent solvents, form a fine powder without crystalline structure, give no salts, and explode on heating, giving iodine vapour and leaving a black residue.

2:4:5-Tri-iodo-1-ethylglyoxaline, when boiled with sodium hydroxide, develops a strong odour of ethylcarbamylamine.

Tetraiodoglyoxaline when heated decomposes at 160° into iodine and a black residue, which contains all the nitrogen, and about 25% of the iodine of the original substances. This iodine is not removed until the residue is heated to 400°, when it has the composition  $C_3N_2$ . At a temperature near a red heat, above 500°, this in turn decomposes to carbon and nitrogen. This behaviour is similar to that of cyanuric iodide,  $C_3N_3I_3$ , studied by Klason (Abstr., 1886, 1001).

Three derivatives of histidine, namely, benzoyl- and *p*-nitrobenzoyl-histidine and *l*-histidine anhydride, have been iodised; in each case two iodine atoms become attached to carbon in the glyoxaline nucleus, and the compounds are regarded as derivatives of the unknown di-iodo-



Preparation of the *disilver* salt in the case of *tetraiodohistidine anhydride* proved the nitrogen groups to have no iodine attached to them.

Iodine is the more easily introduced into glyoxalines the more basic they are; thus, 5-methylglyoxaline decolorises nearly 7/10 mol. iodine, glyoxaline only about 1/7 mol. Histidine and histidine anhydride behave much as glyoxaline, but the introduction of acyl residues, causing the bases to react acid towards litmus, almost destroys the power of taking up iodine.

The amount of iodine absorbed by surine corresponds almost exactly with that required by the histidine contained in surine.

Tri-iodoglyoxaline in small doses causes a marked quickening of the reathing and of the pulse.

2:4:5-Tri-iodo-1-ethylglyoxaline forms colourless crystals, m. p. 41—142°.

1:2:4:5-Tetraiodoglyoxaline is a colourless or yellowish-grey, odourless powder, decomp. 160°.

4:5-Di-iodo-2-methylglyoxaline crystallises in centimetre-long, thin, astrous prisms, m. p. 199°; it dissolves in acids or alkalis, forming salts.

1:4:5-Tri-iodo-2-methylglyoxaline is a greyish-yellow, insoluble powder, decomp. 160°.

1-Iodo-2:4:5-trimethylglyoxaline is a cream-coloured, dust-like powder, m. p. 134° (decomp. and blackening).

Benzoylhistidine has m. p. 249° (Fäinkel: 230°).

Benzoyldi-iodohistidine is a colourless, chalk-like powder, m. p. 61—164° in an evacuated tube.

*p*-Nitrobenzoyldi-iodohistidine has m. p. 172° (decomp.). Like the

foregoing, it gives an orange-red coloration with diazobenzenesulphonic acid and sodium carbonate, and forms a *silver* salt.

*Tetraiodohistidine anhydride* crystallises from alcohol in aggregates of minute, rectangular plates, m. p. 240° (in an evacuated tube) to a dark liquid.

The compound is amphoteric, and dissolves in both acids and alkalis; it reacts with diazobenzenesulphonic acid, dissolves in cold, strong acids without decomposition, and on heating with sulphuric acid gives iodine vapour at 150°. The *disilver* salt is at first colloidal, but subsequently flocculent; it explodes on heating.

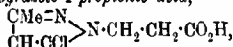
Reduction by means of sulphites converts tetraiodohistidine anhydride into the *di-iodo*-compound; this forms a microcrystalline powder, m. p. 245° (decomp.).

Iodine is without action on alanine anhydride.

E. F. A.

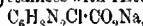
**Carboxylic Derivatives of 3-Methyl- and 3-Phenyl-5-chloro-pyrazole.** AUGUST MICHAELIS and OMAR SCHMIDT (*Ber.*, 1910, 43, 2116—2120).—Only a few pyrazole compounds containing acid groups attached to N have been prepared previously (compare Thiele and Heuser, *Abstr.*, 1896, i, 340). Such compounds can be obtained by condensing the sodium derivatives of 5-chloro-3-methyl- and 5-chloro-3-phenyl-pyrazole with the esters of halogenated fatty acids.

*5-Chloro-3-methylpyrazole-1-propionic acid*,



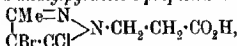
prepared by heating 5-chloro-3-methylpyrazole and ethyl  $\beta$ -iodopropionate with alcoholic sodium ethoxide on the water-bath for several hours, forms compact crystals, m. p. 94°. When heated above its m. p., the acid yields 5-chloro-3-methylpyrazole and acrylic acid.

The ammonium salt crystallises with 1EtOH; the sodium salt,



forms small needles; the barium salt,  $(\text{C}_6\text{H}_5\text{N}_2\text{Cl}\cdot\text{CO}_2)_2\text{Ba}\cdot 3\text{H}_2\text{O}$ , crystallises in colourless plates; the silver salt forms a curdy precipitate; the ethyl ester,  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}\cdot\text{CO}_2\text{Et}$ , forms a pale yellow oil; the methiodide,  $\text{C}_6\text{H}_5\text{N}_2\text{Cl}\cdot\text{CO}_2\text{H}\cdot\text{MeI}$ , forms colourless prisms, m. p. 142°, and the methiodide of the ester has m. p. 136°.

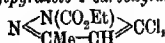
*5-Chloro-4-bromo-3-methylpyrazole-1-propionic acid*,



obtained by brominating the previous acid in glacial acetic acid, forms compact crystals, m. p. 113°.

*5-Chloro-3-methylpyrazole-1-acetic acid* crystallises in colourless needles, m. p. 199°; the ammonium salt crystallises with 1EtOH; the sodium with 2.5H<sub>2</sub>O, and the barium with 5H<sub>2</sub>O. The ethyl ester is a pale yellow oil; the methiodide has m. p. 156°, and the methiodide of the ethyl ester, m. p. 130°. *5-Chloro-4-bromo-3-methylpyrazole-1-acetic acid*,  $\text{C}_6\text{H}_5\text{N}_2\text{ClBr}\cdot\text{CO}_2\text{H}$ , crystallises in nacreous plates, m. p. 197°.

*Ethyl 5-chloro-3-methylpyrazole-1-carboxylate*,



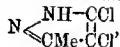
is a colourless oil, b. p.  $127^{\circ}/18$  mm.; the free acid cannot be isolated, as it decomposes immediately into 5-chloro-3-methylpyrazole and carbon dioxide.

5-Chloro-3-phenylpyrazole-1-acetic acid,  $C_{10}H_8N_2Cl \cdot CO_2H$ , forms colourless needles, m. p.  $166^{\circ}$ . The sodium salt crystallises with  $4\frac{1}{2}H_2O$ , and the barium salt with  $7H_2O$ . Its 4-bromo-derivative,  $C_{10}H_7N_2ClBr \cdot CO_2H$ , forms colourless needles, m. p.  $169^{\circ}$ .

J. J. S.

**Pyridines of 1:3-Dimethylpyrazolone.** AUGUST MICHAELIS and AUGUST LACHWITZ (*Ber.*, 1910, 43, 2106—2115).—5-Chloro-3-methyl-

pyrazole,  $N \begin{smallmatrix} \text{NH} \cdot \text{CCl} \\ \diagdown \text{CMe} \cdot \text{CH} \end{smallmatrix}$ , prepared by the action of phosphoryl chloride on 3-methylpyrazolone at  $150^{\circ}$ , forms needles or rhombic crystals, m. p.  $116^{\circ}$ , b. p.  $258^{\circ}$ , and when heated at  $140^{\circ}$  for six hours with phosphorus pentachloride, yields 4:5-dichloro-3-methylpyrazole,

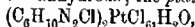


which crystallises in felted needles, m. p.  $128^{\circ}$ , and is insoluble in acids. 5-Chloro-4-bromo-3-methylpyrazole,  $C_4H_4N_2ClBr$ , obtained by the action of bromine on a glacial acetic acid solution of the 5-chloro-derivative, crystallises in glistening needles, m. p.  $140^{\circ}$ , and yields a perbromide,  $C_4H_4N_2ClBr_3$ , m. p.  $186^{\circ}$ . 5-Chloro-4-iodo-3-methylpyrazolone,

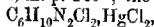


also forms glistening needles, m. p.  $152^{\circ}$ . 5-Chloro-1-benzenesulphonyl-3-methylpyrazolone,  $N \begin{smallmatrix} \text{N}(\text{SO}_2\text{Ph}) \\ \diagdown \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{CCl}$ , forms colourless crystals, m. p.  $67^{\circ}$ , and with bromine yields the 4-bromo-derivative, m. p.  $117^{\circ}$ .

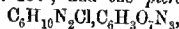
5-Chloro-1:3-dimethylpyrazole methiodide,  $\text{NMeI} \begin{smallmatrix} \text{NMe} \cdot \text{CCl} \\ \diagdown \text{CMe} \cdot \text{CH} \end{smallmatrix}$ , prepared by heating 5-chloro-3-methylpyrazole with methyl iodide and alcohol at  $100^{\circ}$ , crystallises in colourless needles, m. p.  $240^{\circ}$ . The methobromide has m. p.  $276^{\circ}$ , and the methochloride contains  $3H_2O$  and has m. p.  $230^{\circ}$ , or  $252^{\circ}$  anhydrous; the platinumchloride,



forms red, compact crystals, m. p.  $243^{\circ}$ ; the mercurichloride,



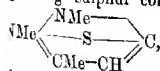
colourless plates, m. p.  $136^{\circ}$ , and the picrate,



pale yellow needles, m. p.  $132^{\circ}$ .

5-Chloro-3-methyl-1-ethylpyrazole ethiodide forms colourless plates, m. p.  $186^{\circ}$ .

Silver oxide reacts with an aqueous solution of the methiodide, or methochloride, yielding 2:5-oxido-1:2:3-trimethylpyrazole (1-methyl-antipyrine) (compare Knorr, *Abstr.*, 1906, i, 893). The corresponding sulphur compound, 2:5-sulphido-1:2:3-trimethylpyrazole,



obtained by the action of sodium sulphide on the methiodide or methochloride, contains  $1\frac{1}{2}H_2O$ , which it loses at  $100-105^{\circ}$ ; when anhydrous it has m. p.  $147^{\circ}$ , and hydrated, m. p.  $83^{\circ}$ .

The *hydrochloride*,  $C_6H_{10}N_2S \cdot HCl$ , forms large prisms, which deliquesce in the air; the *platinichloride*,  $(C_6H_{10}N_2S)_2H_2PtCl_6$ , forms a reddish-brown, amorphous powder, which decomposes at  $320^\circ$ ; the *hydriodide* forms slender needles, m. p.  $168^\circ$ .

4-Bromo-2:5-sulphido-1:2:3-trimethylpyrazole,  $C_6H_8N_2BrS$ , prepared from the methiodide of 5-chloro-4-bromo-3-methylpyrazole, crystallises in colourless needles, m. p.  $221^\circ$ . The *trioxide*,  $C_6H_8O_3N_2S$ ,

can be prepared by passing chlorine into an aqueous solution of sulphido-1:2:3-trimethylpyrazole, or by the action of sodium sulphite on the methiodide of 5-chloro-1:3-dimethylpyrazole, and crystallises in colourless needles, m. p.  $237^\circ$  (decomp.). The thiopyrine combines with methyl iodide at the ordinary temperature, yielding the *methiodide*,  $NMeI \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{SMe}$ , as pale yellow, compact crystals, m. p.

$199^\circ$ ; the corresponding *methochloride* contains  $2H_2O$ , and has m. p.  $130^\circ$ ; the *platinichloride* forms golden-yellow needles, m. p.  $225^\circ$ . When the thiopyrine or its methiodide is distilled, the  $\psi$ -compound,

5-methylthiol-1:3-dimethylpyrazole,  $N \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{SMe}$ , is obtained as a colourless oil, b. p.  $243^\circ$ ; its *platinichloride* crystallises in golden-yellow plates, m. p.  $264^\circ$ , and its *nitroso-derivative*,  $N \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{C} \cdot \text{NO} \end{smallmatrix}$ ,

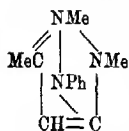
forms dark green, glistening needles. When oxidised with permanganate in acetic acid solution, the  $\psi$ -compound yields a *sulphone*,  $C_6H_{10}O_2N_2S$ , as colourless, glistening needles, m. p.  $121^\circ$ .

2:5-Anilo-1:2:3-trimethylpyrazole (1-methylanilopyrine), annered formula, obtained by heating the methiodide or methochloride of chlorodimethylpyrazole with aniline at  $124^\circ$  for two hours, forms compact crystals, m. p.  $82^\circ$ ; it is strongly alkaline, and rapidly absorbs carbon dioxide. The *hydrochloride*,  $C_{12}H_{16}N_4Cl \cdot 2H_2O$ , forms compact, colourless needles, m. p.  $238^\circ$  when anhydrous; the *platinichloride* forms golden-yellow needles, m. p.  $207^\circ$ ; the *picrate*,  $C_{12}H_{16}N_4 \cdot C_6H_3O_7N_3$ , yellow prisms, m. p.  $129^\circ$ ; the *chromate*,  $(C_{12}H_{16}N_4)_2H_2Cr_2O_7$ , orange-yellow plates, m. p.  $171^\circ$ , and the *carbonate*,  $C_{12}H_{16}N_4 \cdot H_2CO_3$ , a colourless powder, m. p.  $102^\circ$  (decomp.).

The *methiodide*,  $NMeI \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NMePh}$ , forms slender, colourless needles, m. p.  $200^\circ$ , and the *propiodide*,  $C_{12}H_{15}N_3 \cdot C_3H_7I$ , compact crystals, m. p.  $176^\circ$ . When the methiodide is distilled under reduced pressure it yields the  $\psi$ -compound, 5-methylanilino-1:3-dimethylpyrazole,  $N \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NMePh}$ , as a viscid, colourless oil, b. p.

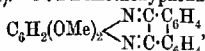
$165^\circ/30$  mm. Its *nitroso-derivative*,  $C_{12}H_{14}ON_4$ , forms dark green, compact crystals, m. p.  $135^\circ$ . When the hydrochloride is distilled under 30 mm. pressure, it yields methyl chloride and 5-anilino-1:3-dimethylpyrazole,  $N \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHPh}$ , m. p.  $95^\circ$ .

2:5-Imino-1:2:3-trimethylpyrazole (1-methyliminopyrine), annered



formula, obtained by heating 5-chlorodimethylpyrazole methochloride with aqueous ammonium hydroxide at 130°, forms a yellow oil, and yields a *hydrochloride* in the form of slender needles, m. p. 258°. The *aurichloride*,  $C_6H_{11}N_2 \cdot HAuCl_4$ , forms golden-yellow plates, m. p. 184°; the *platinichloride*, yellow needles, m. p. 210°. The base absorbs carbon dioxide rapidly. J. J. S.

1:2-Dimethoxyphenanthraphenazine. ILIE J. PISOVSCHI (*Ber.*, 1910, 43, 2137—2144).—1:2-Dimethoxyphenanthraphenazine,



has been synthesised from acetylvanillin by the following series of reactions:  $CHO \cdot C_6H_3(OMe) \cdot OAc \rightarrow CHO \cdot C_6H_3(OMe)(NO_2) \cdot OAc \rightarrow CHO \cdot C_6H_3(OMe)(NO_2) \cdot OH \rightarrow CHO \cdot C_6H_3(OMe)_2 \cdot NO_2 \rightarrow CO_2H \cdot C_6H_3(OMe)_2 \cdot NO_2 \rightarrow NH_2 \cdot CO \cdot C_6H_3(OMe)_2 \cdot NO_2 \xrightarrow{1:2} NH_2 \cdot C_6H_2(OMe)_2 \cdot NO_2 \xrightarrow{3:4} C_6H_2(NH_2)_2(OMe)_2 \rightarrow C_6H_2(OMe)_2 \begin{matrix} \swarrow N:C_6H_4 \\ \searrow N:C_6H_4 \end{matrix}$

A modification of Pschorr and Sumuleanu's method for the preparation of acetylvanillin (*Abstr.*, 1900, i, 178) is described. *adj-o-Nitro-veratraldehyde* is best prepared by methylating *o-nitrovanillin* with methyl sulphate and alkali; it has m. p. 63°, and when oxidised in acetone solution with aqueous permanganate yields *o-nitroveratric acid*, m. p. 203°.

The *chloride*,  $NO_2 \cdot C_6H_3(OMe)_2 \cdot COCl$  [2:3:4:1], forms slender, colourless needles, m. p. 73°, and the *amide*,  $NO_2 \cdot C_6H_3(OMe)_2 \cdot CO \cdot NH_2$ , crystallises from toluene in long, colourless needles, m. p. 172°, and is resistant towards hydrolysing agents.

(*adj*)-3-*Nitro-4-aminoveratrole*,  $NO_2 \cdot C_6H_3(OMe)_2 \cdot NH_2$ , crystallises in red needles, m. p. 74°, and exhibits dichroism. When reduced with iron and acetic acid, it yields *adj-veratrylenediamine*,  $C_6H_3(NH_2)_2(OMe)_2$ , in silver-white plates, m. p. 97°. This base is much more stable than Moureu's *s-veratrylenediamine* (*Abstr.*, 1897, i, 411). The halide salts form colourless needles, but their aqueous solutions have a cherry-red or reddish-violet colour. The base condenses with phenanthraquinone in the presence of acetic acid, yielding 1:2-dimethoxyphenanthraphenazine in yellow, felted needles, m. p. 174—175°. Its dilute solutions have a green fluorescence. The *hydrochloride* and *hydrobromide* are red; the *hydriodide*, brownish-black, and all three are hydrolysed by water.

J. J. S.

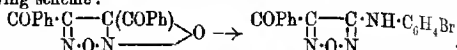
Products of the Action of the Primary Amines on the Dinitrosaclys [Glyoximeperoxides]. II. JACOB BÖSEKEN (*Rec. trav. chim.*, 1910, [ii], 14, 275—292. Compare *Abstr.*, 1898, i, 696).—Wieland and Semper have shown (*Abstr.*, 1904, i, 54; 1908, i, 108) that the dinitrosaclys probably have the endoxyfurazan or furoxan,  $\begin{matrix} C \\ | \\ N \cdot O \cdot N \end{matrix} > O$ , rather than the glyoxime-peroxide configuration,  $\begin{matrix} C \cdot N \cdot O \\ | \\ C \cdot N \cdot O \end{matrix}$ .

The conclusions drawn previously (*Abstr.*, 1898, i, 696) from the



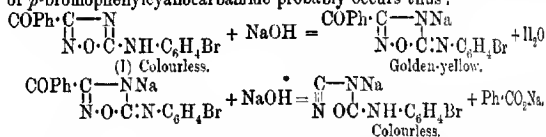
reactions of these compounds are now reconsidered in the light of Wieland and Semper's work.

[With H. COUVERT.]—Diphenyldinitrosacyl, prepared by Holleman's method (Abstr., 1893, i, 205), when heated in ethereal solution with *p*-bromoaniline (2 mols.) gives dark brown needles, decomposing at 126°, of *benzoyl-p-bromoanilino*furazan, probably according to the following scheme:

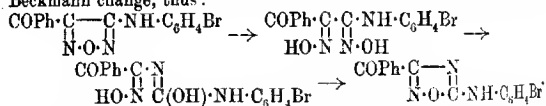


If this furazan is heated on a water-bath with glacial acetic acid, it is transformed into an isomeride, which crystallises in colourless, felted needles, m. p. 208°. This isomeride is not attacked by concentrated sulphuric acid or by nitric acid (D 1.35), and, therefore, the presence of the CN group is very improbable, but it dissolves in potassium ethoxide solution, giving a golden-yellow liquid, which, on heating on a water-bath, becomes colourless, and yields the potassium salt of *p*-bromophenyleyanocarbamide. The free *p*-bromophenyleyanocarbamide forms colourless needles, decomposing above 325°.

The production of a substituted nitrile by intramolecular change has been observed by Claisen (Abstr., 1904, i, 14; 1909, i, 185), by Wieland and Hess (Abstr., 1909, i, 369), by Wolff (Abstr., 1895, i, 192), and by Hantzsch and Urbahn (Abstr., 1895, i, 393). From its resemblance to the reactions described by these authors, the formation of *p*-bromophenyleyanocarbamide probably occurs thus:



The author considers that the colourless isomeride obtained from benzoyl-*p*-bromoanilino-furazan has the constitution of *benzoyl-p-bromoanilino-αβ'-furodiazole* (I), and is formed from the furazan by a partial Beckmann change, thus:



*p*-Bromophenyleyanocarbamide cannot be recrystallised from water owing to partial decomposition. It is decomposed by dilute hydrochloric acid according to the equation:  $\text{C}_6\text{H}_4\text{ON}_3\text{Br} + 2\text{H}_2\text{O} = \text{C}_6\text{H}_4\text{Br} \cdot \text{NH}_2 + \text{CO}_2 + \text{CO}(\text{NH}_2)_2$ . From conductivity measurements the value  $2.4 \times 10^{-4}$  was obtained for its dissociation constant ( $K$ ), whilst a colorimetric comparison (using Congo-red) with hydrochloric acid of different strengths gave  $1.8 \times 10^{-4}$ .

A solution of the potassium salt of *p*-bromophenyleyanocarbamide gives a white, flocculent precipitate with silver nitrate, stable in the light and soluble in ammonia. The ammoniacal solution deposits small, brilliant crystals of the silver ammonia derivative,  $\text{C}_6\text{H}_4\text{ON}_3\text{BrAgNH}_3$ , which are not acted on by light, but lose ammonia when heated.

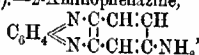
Addition of a solution of copper sulphate to a solution of potassium *p*-bromophenylcyanocarbamide gives a yellowish-green, crystalline precipitate of the copper salt. The latter is a very sensitive reaction for all cyanocarbamides.

When the potassium salt is warmed at 50° with sulphuric acid or hydrogen peroxide (1.5 mols.) and a little potassium hydroxide solution (compare Radziszewski, *Abstr.*, 1885, 496; Peski, *Abstr.*, 1909, i, 647), *p*-bromophenylthiuret,  $C_6H_4Br \cdot NH \cdot CO \cdot NH \cdot CO \cdot NH_2$ , is formed, which crystallises in long needles decomposing at 230° (approx.).

Similarly, when heated in a sealed tube at 100° with ammonium sulphide, the potassium salt is converted into *p*-bromophenylthiobiuret,  $C_6H_4Br \cdot NH \cdot CO \cdot NH \cdot CS \cdot NH_2$ , which crystallises in long, silky needles, soluble in strong alkalis, from which it is precipitated by carbon dioxide. This thiobiuret has an extremely bitter taste, and loses sulphur when treated with ammoniacal silver or copper solutions.

E. H.

**Aminophenazines.** ALFRED WOHL and MARTIN LANOE (*Ber.*, 1910, 43, 2186—2188).—2-Aminophenazine,



is formed when a mixture of *o*-nitroaniline, aniline hydrochloride, and finely-powdered zinc chloride is heated at 180—185° for half an hour. The same product is formed when formanilide is used in place of aniline hydrochloride. The m. p. of the pure product is 288° (corr.), not 274°.

Aminonaphthaphenazine, obtained by heating *o*-nitroaniline,  $\alpha$ -naphthylamine, and zinc chloride at 150—180°, crystallises from xylene in yellowish-brown, glistening prisms, m. p. 294° (decomp.).

When substituted anilines are used instead of aniline or  $\alpha$ -naphthylamine, the yields of phenazines are small.

J. J. S.

**Triazole and Tetrazole from Azoimide.** OTTO DIMROTH and GUSTAV FESTER (*Ber.*, 1910, 43, 2219—2223).—Azoimide reacts with acetylene when heated in acetone solution for seventy hours at 100°

in sealed tubes, forming 1:2:3-triazole,  $NH \begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{N} = \text{N} \end{array}$ . This was identified by methylation of the silver salt to 1-methyl-1:2:3-triazole, which forms a very characteristic aurichloride, m. p. 160°.

Similarly, azoimide combines with hydrogen cyanide when heated for two to three days at 100° in alcoholic solution to form tetrazole, and this affords the best method of preparing tetrazole.

Phenylazoimide combines with acetylene when heated in acetone solution for forty hours to 1-phenyl-1:2:3-triazole. Phenylazoimide, however, does not condense with hydrogen cyanide or cyanogen, or with ethyl cinnamate.

E. F. A.

**The Oxidation of Some Azo-derivatives to the Corresponding Azoxy-compounds.** ANGELO ANOELI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 793—795).—Only a few instances of the oxidation of azo-

azoxy-compounds are described in the literature, and some of these are doubtful.

If hydrogen peroxide is added to a solution of azobenzene in acetic acid, pure azoxybenzene is obtained in a few days. The reaction closely resembles the conversion of tertiary amines into their oxides by the same reagent. This result, taken together with other reactions studied by the author, favours the constitution  $\begin{array}{c} \text{R} \cdot \text{N} \cdot \text{N} \cdot \text{R} \\ | \\ \text{O} \end{array}$  for the azoxy-compounds.

C. H. D.

**Researches on Benzidine Formation.** HENRI DUVAL (*Bull. Soc. chim.* 1910, [iv], 7, 727—732. Compare this vol., i, 559, 588).—2:3.

*Hydrazodiphenylethane*,  $\text{C}_6\text{H}_5 \begin{array}{c} \text{NH-NH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C}_6\text{H}_5$ , prepared by reducing 2:2'-azodiphenylethane (Abstr., 1909, i, 747) with zinc dust and barium hydroxide in aqueous alcoholic solution, forms yellowish-white crystals, m. p.  $151^\circ$ , which give only very small quantities of a colourless, nitrogenous, weakly basic, crystalline substance, m. p.  $230^\circ$ , when treated with hydrochloric acid. Like the corresponding methane derivative, 2:2'-azodiphenylethane, when reduced with a boiling hydrochloric acid solution of stannous chloride, gives 2:2'-diaminodiphenylethane, described by Busch and Weiss (Abstr., 1900, i, 699). The conclusion is drawn that the reactions in the diphenyl, diphenylmethane, and diphenylethane series are essentially different from those in the benzene series, since in the former cases the benzidine formation does not occur.

E. H.

**Changes in the Physical Conditions of Colloids. X. Action of Organic Bases and Amphoteric Electrolytes on Albumin.** HANS HANDOVSKY (*Biochem. Zeitsch.*, 1910, 25, 510—538. Compare this vol., i, 344).—The influence of bases and amphoteric electrolytes on the formation of albumin salts has been investigated by means of viscosity measurements. The comparative data indicate that the hydrolysis of the albumin salts increases as the dissociation constant of the added base diminishes. From the observations with amphoteric electrolytes it is found that variations of the basic dissociation constant between  $10^{-12}$  and  $10^{-15}$  have little effect on the formation of albumin ions in comparison with variations in the acid dissociation constant. Amphoteric electrolytes with small basic dissociation constant and higher acid dissociation constant are most favourable to the formation of neutral albumin complexes.

H. M. D.

**General Protein Chemistry. I. The Coagulation of Denatured Albumin, Considered as a Function of the Hydrogen Ion Concentration and of the Salts.** LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1910, 27, 38—52).—Experiments were carried out to test the Helmholtz-Bredig theory that surface-tension reaches a maximum and precipitation follows most readily when the protein particles carry no charge, that is, are immersed in a liquid of certain definite hydrogen ion concentration. For this purpose, dialysed albumin was denatured by heating. Mixtures of acetic acid and

sodium acetate in varying quantities were added to the turbid mixture, and the mixture producing the optimum sedimentation effect was noted. The hydrogen ion concentration of this solution could be readily determined. The rate of sedimentation varied when salts other than sodium acetate were employed. It was found that the isoelectric constant of serum albumin was  $0.3 \times 10^{-5}$ , and the relative acidity  $1.6 \times 10^3$ . The sedimentation rate is, in the first place, a function of the hydrogen ion concentration, and, in the second place, a function of the total content in electrolytes. The sedimentation rate is at a maximum when the  $H^+$  concentration is that of the isoelectric point, and is larger the poorer the solution is in total electrolytes.

S. B. S.

**Hæmocyanin of *Limulus polyphemus*.** CARL ALSBERG and E. D. CLARK (*J. Biol. Chem.*, 1910, 8, 1—8).—Hæmocyanin does not appear to be uniformly the same substance in all parts of the animal kingdom. That obtained from *Limulus* blood differs from that described by Henze from *Octopus* blood in percentage composition, in its precipitability by dialysis, by full saturation with magnesium sulphate, by half saturation with ammonium sulphate, in not having been crystallised, and in being more readily broken up by acid with liberation of the copper. No copper compound analogous to hæmatin was formed. In its globulin-like characters, the *Limulus* hæmocyanin thus resembles that described by Halliburton, who worked mainly with Crustacean blood. The following table of percentage composition is given:

	C.	H.	N.	S.	Cu.	O.
<i>Octopus</i> .....	53.66	7.33	16.09	0.86	0.33	21.68
<i>Limulus</i> .....	48.94	7.10	16.18	1.56	0.28	25.94

W. D. H.

**Guanylic Acid.** IVAR BANG (*Biochem. Zeitsch.*, 1910, 26, 293—311).—The protein was prepared by extracting pancreas with hot water and adding oxalic acid to the extract. This was dissolved in potassium hydroxide solution, and to this was added solid ammonium sulphate, so that the solution was  $\frac{1}{2}$  to  $\frac{2}{3}$  saturated (260 grams of salt to 500 c.c. of solution). The filtrate from the precipitated protein was diluted, and the guanylic acid precipitated from the liquid thus obtained either by copper acetate or copper sulphate and ammonia. The copper salt was decomposed by hydrogen sulphide, and the filtrate from the copper sulphide precipitated by 25% hydrochloric acid and twice the volume of alcohol. The precipitate was washed with water, and as the acid guanylic salt dissolved, acid was added to the washings. Four to five grams of guanylic acid were thus obtained from five organs of an ox. On hydrolysis, this guanylic acid yielded guanine, contaminated by a little xanthine, which the author succeeded in showing was a secondary product formed from the first-named base, phosphoric acid, and a pentose, the quantity of which was estimated by the author's hydroxylamine method, and amounted to 41% of the guanylic acid hydrolysed. The author discusses the formula of guanylic acid and its relationship to inosic and thymonucleic acids.

S. B. S.

**The Optical Rotation of Gelatin.** HANS TRUNKEL (*Biochem. Zeitsch.*, 1910, 26, 493—513).—The optical activity of fresh gelatin solutions is variable, and reaches a maximum between the twelfth and hundred and twentieth hour. On warming, the original activity is restored. The activity is also dependent on temperature, decreasing with increasing temperature to 35°, when a maximum is attained. The optical activity is not proportional to the concentration; the weaker the concentration the smaller is the dextrorotation. The deviation is the smaller the longer and higher the solution is heated before taking the observation. The rotation of  $\beta$ -gelatin is appreciably smaller than that of the  $\alpha$ -variety. The combining power for tannin of gelatin diminishes on keeping at first rapidly, and then more slowly; the rotatory power shows the opposite action (increasing rapidly at first, etc.). These phenomena are to be ascribed to a change in the condition known as "hysteresis," which the author discusses.

S. B. S.

**The Anti-protease of Yeast Juice.** EDUARD BUCHNER and HUGO HAEHN (*Biochem. Zeitsch.*, 1910, 26, 171—198).—It has been already shown that expressed yeast juice when kept loses first the co-enzyme and finally the zymase, which latter cannot be subsequently regenerated on addition of the former. The destruction of the zymase is due to an endotryptase. If boiled juice is added to the zymase, however, it can be preserved from destruction, owing to the fact that the boiled juice contains in addition to the co-enzyme an anti-protease which protects the coagulable proteins from the action of the endotryptase. This anti-protease also protects gelatin from liquefaction by endotryptase, and prevents the digestion of caseinogen by the same ferment. It acts also as an anti-substance to trypsin and pepsin. It is not identical with the co-enzyme, for the latter can be destroyed by heating yeast juice for several hours, or by the action of dilute acids at 100°, or by the action of alkali at 37°; under these conditions the anti-protease remains intact. The authors have not yet succeeded in separating chemically the anti-protease from the co-enzyme. Both are destroyed by lipase. The anti-protease is not a simple acid which inhibits the action of endotryptase, and as the anti-proteolytic action of the boiled juice remains intact after neutralisation, and neither is it a simple amino-acid, as substances do not exert any marked anti-action to endotryptase. Preliminary experiments indicate that it is an organic ester-like substance. The authors draw the conclusion that the anti-protease plays an important part in the life-processes of the yeast. The protective action is probably due to the capacity of the anti-protease to combine with the protein.

S. B. S.

## Organic Chemistry.

**Catalytic Reactions in the Wet Way, Based on the Use of Aluminium Sulphate.** JEAN B. SENDERENS (*Compt. rend.*, 1910, 151, 392—394).—The addition of sand in the classical method for the preparation of ethylene is usually recommended on the ground that it prevents frothing. The present communication contains details of experiments from which it appears that this material acts as a catalyst and enables the reaction to proceed at a lower temperature. Aluminium sulphate, especially that prepared by calcining ammonium alum, is still more effective in this respect. The proportions recommended are 200 c.c. of a mixture of sulphuric acid (2 vols.), 95% alcohol (1 vol.), and 10 grams of anhydrous aluminium sulphate. Without the latter, the mixture yields no ethylene at 138°; with sand it gives 7.5—8 c.c. per minute, and with aluminium sulphate, 32 c.c. per minute.

The use of aluminium sulphate is stated to be advantageous in the industrial preparation of ethyl ether. A mixture of sulphuric acid (3 vols.) and 95% alcohol (4 vols.) with 5% of the sulphate gives ether at 110°, the reaction becoming rapid at 130°. In the absence of a catalyst the evolution of ether is not regular until 140°. The method is not suitable with the higher alcohols, the unsaturated hydrocarbon being produced together with liquid condensation products.

Propylene is conveniently prepared by heating propyl alcohol (4 vols.) with sulphuric acid (3 vols.) and 5% of anhydrous aluminium sulphate at 100—110°. The gaseous product contains 95% of propylene.

W. O. W.

**Preparation of Glyceryl Mono- and Di-bromohydrins.** P. CARRÉ (*Bull. Soc. chim.*, 1910, [iv], 7, 835—836).—Glyceryl α-bromohydrin, h. p. 134°/16 mm., is best prepared by diluting glycerol (200 grams) with water (60 grams), passing in hydrogen bromide (162 grams), warming the mixture in a closed vessel at 100° during five to six hours, and distilling the product under reduced pressure, the fraction boiling at 125—160°/16 mm. being collected and re-distilled. The α-dibromohydrin (b. p. 105°/16 mm.) is obtained in a yield of 55 to 60% of the theoretical by warming glycerol (185 grams) to 100°, passing in hydrogen bromide (325 grams), and heating the mixture at 100° during five to six hours. The fraction boiling at 100—120°/16 mm. is collected and re-distilled. Both products are colourless when freshly distilled, but become coloured on exposure to light.

T. A. H.

**Solubility of Ethyl Ether in Water.** YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 21—35).—The ether used had b. p. 34.55°/761.2 mm. The relation between the refractive index and the composition of various mixtures of ether and water at 20° was first determined. It was found that the difference (Δ) between the angle of

refraction of water and the solution of ether in water is a linear function of the number of grams ( $x$ ) of ether contained in 100 grams of the solution, as expressed by the formula  $\alpha = 0.0946\Delta$ .

In order to determine the solubility of ether in water at different temperatures, water was shaken with excess of ether in a tap funnel surrounded by a water jacket. When saturation was complete, the two layers were allowed to separate, and small portions of the lower layer run off into weighed quantities of water contained in stoppered flasks, the quantity of water being so regulated that a homogeneous solution was obtained at 20°. The weights of the separate portions of the lower layer were determined by difference. The angle of refraction of the homogeneous solution was then measured at 20°, and its composition determined by means of the formula given above; the composition of the saturated solution from which it was prepared could then be calculated.

The following results were obtained from the smoothed curve,  $x$  being the number of grams of ether dissolved in 100 grams of water in the saturated solution.

Temp. ...	0°	5°	10°	15°	20°	25°	30°
$x$ .....	13.13	11.18	9.55	8.22	7.03	6.13	5.39

T. S. P.

**Preparation of Chloroacetyl Chloride from Dichlorovinyl Ether.** CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 222194).—When dichlorovinyl ether is saturated with dry hydrogen chloride, kept for twenty-four hours at the ordinary temperature, and then very gradually heated to boiling, *ethyl trichloroethyl ether*,  $\text{CH}_2\text{Cl}\cdot\text{CCl}_2\cdot\text{OEt}$ , is formed; this on distillation is readily decomposed into ethyl chloride and chloroacetyl chloride (b. p. 105°):  
 $\text{CHCl}\cdot\text{CCl}\cdot\text{OEt} + \text{HCl} \rightarrow \text{CH}_2\text{Cl}\cdot\text{CCl}_2\cdot\text{OEt} \rightarrow \text{EtCl} + \text{CH}_2\text{Cl}\cdot\text{COCl}$   
 F. M. G. M.

**Preparation of the Anhydrides of Fatty Acids from their Salts.** TH. GOLDSCHMIDT (D.R.-P. 222236).—The preparation of aliphatic paraffin anhydrides by treating the salts of the acids with sulphur chloride has previously been described (Abstr., 1903, i, 309); it is now found that the reaction takes place if an intimate mixture of dry powdered sulphur and the sodium (or calcium) salt of the acid is treated with chlorine gas at a temperature of  $-24^\circ$  with continual stirring:  $8\text{C}_2\text{H}_5\text{O}\cdot\text{ONa} + \text{S} + 6\text{Cl} = 6\text{NaCl} + \text{Na}_2\text{SO}_4 + 4(\text{C}_2\text{H}_5\text{O})_2\text{O}$ .

The mixture is then kept at the ordinary temperature, warmed to 90°, and subsequently distilled in a vacuum. F. M. G. M.

**Preparation of  $\beta$ -Methyladipic Acid.** FARBENFABRIKEN VON FRIEDR. BAYER & Co. (D.R.-P. 221849).—The technical preparation of  $\beta$ -methyladipic acid may be conveniently carried out by oxidising 4-methylcyclohexanol with boiling concentrated nitric acid to 4-methylcyclohexanone; this intermediate product is then treated with potassium permanganate in alkaline solution, separated from hydrated manganese oxide, and the solution acidified, when a good yield of  $\beta$ -methyladipic

is obtained; it finds employment in the preparation of dyes and in pharmacology.

F. M. G. M.

**Preparation of Organic Aluminium Compounds.** ~~FAUST~~ SCHLIEMANN'S EXPORT-CERESIN-FABRIK (D.R.-P. 221888).—Aluminium salts of mineral waxes may be obtained by treating the raw or purified waxes with aluminium salts, metallic aluminium, or aluminium hydroxide in the presence of an alkali, the function of which is to hydrolyse the esters of the fatty acids; the aluminium may combine with one, two, or three equivalents of the acid. A salt obtained from a pure wax containing 70% wax acid yielded an *aluminium montanate* of deep yellow colour, m. p. 93–95°, and giving a clear solution in hot petroleum. These compounds are employed as preservatives.

F. M. G. M.

**Preparation of Ammonium Hydrogen *l*-Tartrate.** ANDRÉ KLING (*Bull. Soc. chim.*, 1910, [iv], 7, 774–776).—In connexion with the author's process for the estimation of tartaric acid as calcium racemate (this vol., ii, 359), a process for the preparation of ammonium hydrogen *l*-tartrate, based on the observations of Holleman (Abstr., 1898, i, 515; ii, 545) and Marekwald (Abstr., 1896, i, 207), is described. Ordinary tartric acid is racemised by boiling it with sodium hydroxide solution, and the resulting racemic acid precipitated as the calcium salt. From this, racemic acid is regenerated, and the *l*-acid separated by means of cinchonine. From the cinchonine salt, the *l*-acid is recovered as ammonium hydrogen tartrate in the usual way, and freed from a trace of *d*-acid by fractional precipitation with calcium acetate, until the precipitate formed consists solely of crystals of calcium *l*-tartrate. The filtrate on concentration furnishes crystals of the desired salt. Illustrations of the crystals of calcium *l*-tartrate and racemate are given.

T. A. H.

**Ozo-salts of Titanium.** ARRIGO MAZZUCHELLI and ENRICO PANTANELLI (*Gazzetta*, 1910, 40, i, 666–682. Compare Abstr., 1909, i, 631).—The complex potassium ozotitanotartrate previously described (*loc. cit.*) crystallises with 9H<sub>2</sub>O, not with 10H<sub>2</sub>O, as there stated owing to a printer's error in the original paper.

R. V. S.

**Preparation of Acraldehyde.** JEAN B. SENDERENS (*Compt. rend.*, 1910, 151, 530–532. Compare this vol., i, 649).—Anhydrous or hydrated aluminium sulphate effects the catalytic dehydration of glycerol at 105–110°, producing acraldehyde. The large amount of potassium hydrogen sulphate commonly employed in the preparation of this substance from glycerol is unnecessary, since the salt acts as a catalyst. By heating 250 grams of glycerol with 10 grams of potassium hydrogen sulphate for three hours at a temperature not exceeding 110°, 130–140 c.c. of liquid are obtained, which, on re-distillation, furnishes 34–38 c.c. of acraldehyde. The yield is somewhat smaller than that obtained in the usual way, but the product is more stable, and polymerises less rapidly.

W. O. W.



**Action of Acetic Anhydride and its Homologues on Organo-magnesium Compounds.** H. FOURNIER (*Bull. Soc. chim.*, 1910, [iv], 7, 836—840).—Grignard and Tissier have shown (*Abstr.*, 1906, i, 316) that tertiary alcohols are formed by the action of acetic or benzoic anhydride on magnesium methyl iodide. The author has found, in addition, that ketones are produced in this reaction (*Bull. Soc. chim.*, 1904, [iii], 31, 483; 1906, [iii], 35, 19), and a detailed account of his results are now given.

The anhydride (1 mol.) is dissolved in ether, and to this the magnesium alkyl haloid (1 mol.) is added drop by drop, the mixture being cooled in a bath of ice and salt and continuously agitated. The mixture is set aside during two to three hours, and then poured into ice-cold water. The ethereal extract of this is then shaken with dilute sodium hydroxide solution. The purified ethereal solution contains (1) the ketone formed, (2) the ester corresponding to the acid anhydride employed, and the alkyl radicle of the magnesium compound used, and (3) sometimes the tertiary alcohol. The last is separated by fractional distillation, and the ester is eliminated from the residue by hydrolysis, the alcohol formed being distilled off. The ketone is finally isolated by adding water, extracting with ether, drying the solution, and fractionating. The chief reactions occurring are represented by the following equations:  $(R \cdot CO)_2O + R' \cdot MgBr = R \cdot CO \cdot O \cdot CRR' \cdot O \cdot MgBr + H_2O = MgBr \cdot OH + R \cdot CO_2H + R \cdot CO \cdot R'$ .

With magnesium ethyl bromide, acetic anhydride yields methyl ethyl ketone; with magnesium isobutyl chloride, methyl isobutyl ketone, and with magnesium isoamyl bromide, methyl isoamyl ketone. The reaction has also been investigated for propionic, butyric, isobutyric, isopropylacetic, and heptonic anhydrides with various magnesium alkyl haloids, and the corresponding ketones prepared and identified, usually by means of their semicarbazones. T. A. H.

**Preparation of Methylene Ketones.** FÄRDEFABRIKEN VÖM. FRIEDR. BAYER & Co. (D.R.P. 222551).—The action of formaldehyde on ketones in the presence of alkaline condensing agents yields keto-alcohols, which by the action of condensing agents, such as zinc chloride, sulphuric acid, or sodium hydrogen sulphate, are converted into methylene ketones.

*Methylenacetone*,  $COMe \cdot CH_2 \cdot CH_3$ , b. p.  $80^\circ$ , under the ordinary pressure is prepared by heating ketobutanol (100 parts) with zinc chloride (2 parts). It is a colourless, highly refractive oil with a pungent odour.

*Methylenemethyl ethyl ketone*,  $CH_3 \cdot CH \cdot COEt$ , a colourless oil with a strong odour, b. p.  $96^\circ$ , is similarly prepared. These compounds are employed in pharmacy. F. M. G. M.

**Action of Ultra-violet Light on Certain Carbohydrates.** HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1910, 151, 316—318).—Under the influence of light from a quartz-mercury lamp, levulose undergoes profound decomposition when in aqueous solution, carbon monoxide, carbon dioxide, formaldehyde, and methyl alcohol having been recognised amongst the products. The reaction proceeds more readily in a vacuum than when air is present.

Aldoses do not appear to undergo this degradation. Glycerol and mannitol after exposure to the rays acquire reducing properties.

W. O. W.

**Degradation Experiments with Carbohydrates.** CARL NEUBERG and ELSE HIRSCHBERG (*Biochem. Zeitsch.*, 1910, 27, 327—338).—Attempts were made to prepare *l*-glyceraldehyde. The method employed was to degrade *l*-arabonic acid to *l*-erythrose by the ferric acetate and hydrogen peroxide method of Ruff and Meusser, to oxidise the latter to *l*-erythronic acid by bromine water, and to obtain *l*-glyceraldehyde from the latter both by the ferric acetate and hydrogen peroxide oxidation, and by Neuberg's method by the electrolytic decomposition of the copper salt. The experiments were made possible by the authors' discovery of an easy method for preparing *l*-arabonic acid. Cherry gum was hydrolysed by dilute sulphuric acid, which was then removed. The *l*-arabinose thus formed was not isolated, but the quantity in solution was directly estimated polarimetrically, and then sufficient bromine was added to oxidise it to *l*-arabonic acid, which was then isolated as a calcium salt. On oxidising this to *l*-erythrose, an acid by-product insoluble in alcohol was isolated, and obtained in the form of a brucine salt, which was apparently *l*- $\alpha$ - $\gamma$ -trihydroxybutyrylformic acid,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$ . On attempting to prepare *l*-glyceraldehyde from erythroic acid by both methods mentioned, an analogous *l*- $\alpha$ - $\beta$ -dihydroxypropionylformic acid was also probably formed. Only traces of a glyceraldehyde could be isolated, however, and this was optically inactive.

S. B. S.

**Influence of Boric Acid on the Inversion of Sucrose by the Catalytic Action of Hydrochloric Acid.** KATSUNOSUKE ARAFURU (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 229—236).—Boric acid acts as a positive catalyst on the inversion of sucrose. Löwenthal and Lenssen (*J. pr. Chem.*, 1863, 85, 401) found that it retards the catalytic action of hydrochloric acid, but the author finds that it increases the catalytic action. When the concentration of the hydrochloric acid is kept constant, the accelerating effect of the boric acid increases with its concentration, whereas the influence of the boric acid on the catalytic action of hydrochloric acid is practically independent of the concentration of the latter acid.

T. S. P.

**Constitution of Vicianose: Diastatic Hydrolysis.** GABRIEL BERTHRAND and GUSTAVE WEISWELLER (*Compt. rend.*, 1910, 151, 325—327. Compare this vol., i, 156).—Vicianose, the new sugar from *Vicia angustifolia*, has been hydrolysed by emulsin, and found to furnish dextrose and arabinose in equimolecular proportions. It may therefore be regarded as a disaccharide formed by the union of these two substances.

W. O. W.

**New Observations on Callose.** LOUIS MANGIN (*Compt. rend.*, 1910, 151, 279—283. Compare Abstr., 1890, i, 734).—The tissue of *Urometina corium*, a coriaceous cryptogram, is a substance having the same composition as cellulose, but differing from it in its insolubility in

Schweitzer's reagent and its behaviour towards iodine. Sulphuric acid hydrolyses it with formation of dextrose. From these and other observations the author considers it to consist of practically pure callose.

Like cellulose, callose is met with in different states of aggregation, probably corresponding with different degrees of polymerisation. Tanret's fongose (Abstr., 1898, i, 154) is supposed to be identical with callose.

W. O. W.

**Relations of Callose with Fongose.** CHARLES TANRET (*Compt. rend.*, 1910, 151, 447—449. Compare preceding abstract).—The author denies the identity of callose with fongose (fungose). Callose is insoluble in aqueous alkali hydroxides, but becomes soluble after treatment with dilute sulphuric acid, as described in connexion with the preparation of fongoso. Callose appears to be a more complex substance than fongose, and the relation between the two compounds appears to be similar to that existing between starch and amylose.

W. O. W.

**Celluloses. I.** WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Acad. roy. Belg.*, 1910, 587—589).—On macerating filter paper with concentrated hydrochloric acid at 28°, no reducing substance is produced even after forty hours. If the paper is macerated during sixty-two hours and the mixture then heated at 95—96° during twenty minutes, it becomes brown, but the filtrate does not reduce Fehling's solution. The brownish residue is partly soluble in ammonia, and consists of humic matter. Cotton macerated during forty hours in hydrochloric acid shows no reduction, but after eighty-seven hours at 28.5°, and then ten minutes at 95—96°, shows copious reduction. It dissolves in fuming hydrobromic acid at 29° in a few minutes, and the solution blackens on keeping. Such a solution gives a slight, brownish-black precipitate, partly soluble in ammonia on dilution, and reduces Fehling's solution.

T. A. H.

**Cellulose. I. Hydrocellulose.** H. JENTGEN (*Zeitsch. angew. Chem.*, 1910, 23, 1541—1546).—Hydrocellulose is formed by the action of water vapour on cellulose containing adsorbed acid, the acid acting as a contact catalyst. For the formation of the adsorption product between acid and cellulose, it is necessary that the former be in the so-called molecular condition, that is, dissolved in a non-dissociating medium, such as glacial acetic acid, amyl acetate, ether, etc. The acids generally used are hydrochloric and sulphuric, and also their salts with weak bases, and the velocity of hydrolysis depends on the medium used, of which glacial acetic acid is the best.

Hydrocellulose is not extremely resistant towards acids and bases. At medium concentrations, sulphuric acid causes amyloid formation, stronger acid dissolves it, and the most concentrated acid destroys it. It is soluble in zinc chloride, phosphoric acid, fuming nitric acid, and concentrated ammoniacal copper oxide, in the last-named to 10—15%; it is only very sparingly soluble in Wright's liquid.

Alkalis readily attack hydrocellulose, oxycellulose being formed at

the boiling point. It dissolves in cold sodium hydroxide to the extent of about one-third, the remainder being mercerised. The solution contains hemi-cellulose, which can be precipitated by acids, and also yellow to brown degradation products, which are soluble in water.

T. S. P.

**Colloidal Properties of Starch, Especially its Electrical Transport.** FILIPPO BORTAZZI and C. VICTOROFF (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 7—14. Compare FOUARD, *Abstr.*, 1908, i, 953; MAQUENNE and ROUX, *ibid.*, 1906, i, 547).—The authors confirm the results of the above-named writers. The amylose of starch forms a colloidal solution with water, which is perfectly clear and transparent, but does not dialyse. The solution can be filtered through hardened gelatin under pressure (ultra-filtration). When an electric current is passed through it, no migration is observed. The amylopectin of starch forms with water a suspension, in which the granules are visible under the ultra-microscope. The suspension is the more stable the more alkali it contains, so that dialysis, which removes a part of the alkali, causes a partial precipitation. The solution is precipitated by acids. When subjected to ultra-filtration, the substance does not pass through the gelatin, and thus a separation from amylose can be effected. The two substances can also be separated by precipitating the amylopectin with acid, the amylose being afterwards thrown down by the addition of alcohol to the filtrate. Amylopectin is transported towards the anode in neutral solutions containing only small quantities of electrolytes; when large quantities of the latter are present, or when the solution is alkaline or acid, no transport takes place.

R. V. S.

**Action of (1) Hydracids, (2) Hydrolysing Agents, on Starch.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 515—517, 586—587).—A mixture of starch (3 grams), water (35—40 grams), and concentrated hydrochloric acid (2 c.c.) kept at 14° reduces Fehling's solution slightly after three days and markedly after six days. The action is much more rapid at 100°. Concentrated hydrobromic or hydriodic acid behaves similarly on being kept in contact with starch at the ordinary temperature, and hydrolysis is also effected by hot dilute hydriodic acid.

The following substances dissolved, or suspended, in water also hydrolyse starch: ferric, platinic, auric, and stannous chlorides; chlorine; potassium ferrocyanide, ferricyanide, dichromate, and hydroxide; sodium hydroxide, hydrogen carbonate, and dichromate; ammonium, lithium, barium, strontium, and calcium hydroxides; cupric sulphate; cobalt nitrate; nitric (dilute), chromic (dilute), acetic, tartaric, benzoic, picric, and other organic acids.

T. A. H.

**Synthesis of Agmatine.** ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1910, 68, 170—172. Compare this vol., i, 500).—Agmatine has been synthesised by the following process. Carbon dioxide is passed for fourteen days through a suspension of silver cyanamide in a

solution of tetramethylenediamine pyrocenioriae. The liquid is acidified with sulphuric acid, filtered, and the filtrate mixed with an aqueous solution of silver sulphate until a test portion gives a dark brown precipitate with barium hydroxide. The whole is then neutralised with barium hydroxide, filtered, and the filtrate saturated with barium hydroxide. The dark brown precipitate is washed with water, suspended in dilute sulphuric acid, decomposed with hydrogen sulphide, and the resulting sulphate transformed into the sparingly soluble carbonate.

Agmatine can also be obtained by the direct action of an aqueous solution of cyanamide on tetramethylenediamine, and its constitution as aminobutyleneguanidine,  $\text{NH}_2 \cdot \text{C}(\text{NH}) \cdot \text{NH} \cdot [\text{CH}_2]_3 \cdot \text{NH}_2$ , is confirmed.

J. J. S.

**Attempts to Synthesise  $\alpha$ -Diaminopentan- $\gamma$ -ol.** OTTO MORGENSEN and FRANZ ZERNER (*Monatsh.*, 1910, 31, 777—780).—With the object of preparing large quantities of  $\alpha$ -diaminopentan- $\gamma$ -ol, it was sought to convert *s*-dichlorohydrin by means of potassium cyanide into the dinitrile,  $\text{OH} \cdot \text{CH}(\text{CH}_2 \cdot \text{CN})_2$ , and reduce this compound. Dichlorohydrin (1 mol.) and potassium cyanide (2 mols.) were caused to interact in various ways, but the nitrile was only obtained as a blackish-brown, amorphous, hygroscopic solid, which could not be purified. On hydrolysis, glutamic acid was obtained, of which the copper salt forms a bluish-green, crystalline powder, becoming brown at 250°. Reduction of the crude nitrile by means of sodium and amyl alcohol gave a small quantity of a colourless distillate with an amine-like odour, b. p. 255—270°. *Diaminopentanol picrate*,  $\text{C}_5\text{H}_{14}\text{ON}_2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ ,

decomposes at 272°.

E. F. A.

**Synthesis of Polypeptides. XXXII. (I) Derivatives of Aspartic Acid.** EMIL FISCHER and ALBERT FIEDLER (*Annalen*, 1910, 375, 181—198. Compare Abstr., 1909, i, 887).—In view of the importance of aspartic acid as a constituent of natural proteins, the authors have applied to it the reactions by which glycylglutamyl-diglycine was synthesised from glutamic acid (Fischer, Kropp and Stahlschmidt, *Abstr.*, 1909, i, 368), and have succeeded in preparing a tetrapeptide from 3 mols. of glycine and 1 mol. of aspartic acid, to which the name *glycylaspartylglycylglycine* is assigned.

*Chloroacetyl-L-aspartic acid*,  $\text{CH}_3\text{Cl} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared from chloroacetyl chloride and aspartic acid or asparagine under suitable conditions, is a crystalline powder, which has m. p. 142—143° (decomp., corr.), and  $[\alpha]_D^{20}$  4.19° in aqueous solution, and yields with 25% ammonium hydroxide after three days at the ordinary temperature, *glycyl-L-aspartic acid*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 207° (decomp., corr.),  $[\alpha]_D^{20}$  11.08° in aqueous solution, which crystallises with  $\text{H}_2\text{O}$ . *d- $\alpha$ -Bromoisohexoylglycyl-L-aspartic acid*,  $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prepared from glycyl-L-aspartic acid and *d- $\alpha$ -bromoisohexoyl chloride*, is hygroscopic, has m. p. 119—120° (corr.),  $[\alpha]_D^{20}$  61.35° in alcoholic solution, separates from hot water in short prisms containing  $\frac{1}{2}\text{H}_2\text{O}$ .

and by treatment with ammonium hydroxide as above is converted into *l-leucylglycyl-l-aspartic acid*,  
 $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
 m. p. 239° (decomp., corr.), and  $[\alpha]_D^{20}$  55.10° in aqueous solution.

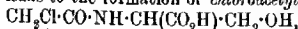
Chloroacetylaspartic acid is treated with acetyl chloride and phosphorus pentachloride in the cold, and an ethereal solution of the resulting crude acid chloride is treated with ethereal ethylglycine at 0°, whereby ethylglycine hydrochloride and *ethyl chloroacetyl-aspartylglycine*,

$\text{CH}_3\text{CH}_2\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ ,  
 are obtained; after the removal of the former by cold water, the latter is purified by hot ethyl acetate and animal charcoal. It separates in colourless needles, has m. p. 176—177° (corr.), and is optically inactive, racemisation having occurred probably during the conversion of the chloroacetyl-aspartic acid into its chloride. *Chloroacetyl-aspartylglycine*, m. p. 142—143° (decomp., corr.), obtained by hydrolysing the preceding ester with *N*-sodium hydroxide at the ordinary temperature, separates from hot water in crystals containing  $\text{H}_2\text{O}$ , is sparingly soluble in cold water, has a strongly acid reaction, and is converted by 25% ammonium hydroxide at 25° in five days into *glycyl-aspartylglycine*,  
 $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
 m. p. 201—2.3° (corr.), an aqueous solution of which becomes dark blue when boiled with copper oxide.

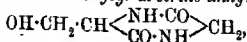
*d*- $\alpha$  Bromoisohexoyl-l-aspartic acid,

$\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  
 m. p. 150° (corr.),  $[\alpha]_D^{20}$  8.10° in aqueous solution, is prepared from aspartic acid and *d*- $\alpha$ -bromoisohexoyl chloride, and is converted by ammonium hydroxide into *l-leucyl-l-aspartic acid*, m. p. 182° (decomp., corr.),  $[\alpha]_D^{20}$  26.92° in aqueous solution, which separates from hot water in slender needles containing  $2\text{H}_2\text{O}$ . C. S.

**Synthesis of Polypeptides. XXXI. (11.) Dipeptides of Serine.** EMIL FISCHER and HANS ROESNER (*Annalen*, 1910, 376, 199—206).—As mixed polypeptides of serine are probably formed by the partial hydrolysis of silk-fibroin, the authors have prepared certain dipeptides of serine which it is hoped may be of use in elucidating the nature of the hydrolytic products of silk-fibroin. The reaction between *r*-serine and chloroacetyl chloride in *N*-sodium hydroxide cooled by a freezing mixture leads to the formation of *chloroacetylserine*,



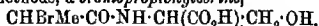
m. p. 122—123° (corr.), which tastes and reacts strongly acid, and is converted by 25% ammonium hydroxide at the ordinary temperature into *glycyl-dl-serine*, m. p. 207° (decomp., corr.), which has a slight acid reaction and gives a deep blue colour when its aqueous solution is warmed with copper oxide. *Glycyl-dl-serine anhydride*,



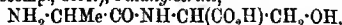
m. p. 227° (corr.), is obtained by saturating a cold methyl-alcoholic suspension of glycylserine with hydrogen chloride and treating the

product in concentrated methyl-alcoholic solution with methyl alcohol saturated with ammonia at 0°.

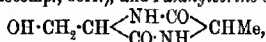
By similar methods, *α-bromopropionylserine*,



m. p. 143° (decomp., corr.), *i-alanyls erine*,



m. p. 209—214° (decomp., corr.), and *i-alanyls erine anhydride*,

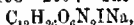


m. p. 228° (corr.), have been obtained.

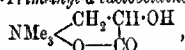
C. S.

**Syntheses of Hydroxybetaines. I. Synthesis of β-Tri-methyl-α-lactobetaine.** ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1910, 68, 1—11).—Attempts have been made to synthesise hydroxybetaines, as compounds of this type, for example, carnitine, novaine, reducto-novaine, and oblitine, occur in nature.

The *basic hydriodide* of *β-trimethyl-α-lactobetaine*,  $\text{C}_{13}\text{H}_{27}\text{O}_6\text{N}_3\text{I}$ , is formed when *isoserine* (Fischer and Leuchs, Abstr., 1902, i, 269) is dissolved in a 7.5% solution of sodium hydroxide in methyl alcohol, mixed with methyl iodide, and the resulting sodium salt decomposed with hydriodic acid. It crystallises from 96% alcohol in compact, transparent prisms, m. p. 198—200°. The *sodium salt*,

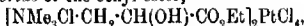


crystallises from 96% alcohol in slender, glistening needles, m. p. 203—206°. The *basic hydrochloride*,  $\text{C}_{13}\text{H}_{27}\text{O}_6\text{N}_3\text{Cl}$ , obtained by the action of silver chlorido on an aqueous solution of the hydriodide, crystallises in slender needles, m. p. 200°. The *normal hydriodide*,  $\text{C}_6\text{H}_{14}\text{O}_3\text{NI}$ , has m. p. 78—80°, and when crystallised from alcohol yields the basic salt. The *normal hydrochloride*,  $\text{C}_6\text{H}_{14}\text{O}_3\text{NCl}$ , has m. p. 155—158°; the *platinichloride*,  $\text{C}_{13}\text{H}_{25}\text{O}_6\text{N}_3\text{PtCl}_6$ , crystallises from 50% alcohol. *β-Trimethyl-α-lactobetaine*,



forms hygroscopic needles, m. p. 203° (decomp.).

The *platinichloride* of the ethyl ester,



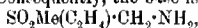
crystallises from aqueous alcohol in hexagonal prisms, which decompose at 235°.

Trimethylamine and β-chlorolactic acid yield carbon dioxide, acetaldehyde, and trimethylamine hydrochloride. J. J. S.

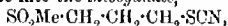
**Cheirolin, the Thiocarbimide in Wall-flower Seeds.** Its **Synthesis and Degradation.** WILHELM SCHNEIDER (*Annalen*, 1910, 375, 207—254. Compare Abstr., 1909, i, 118, 826).—A better method than Wagner's (Abstr., 1908, i, 202) for the isolation of cheirolin from wall-flower seeds is described. The finely ground seeds are extracted with ether, which removes the greater part of the oily constituents, but only a trace of cheirolin. The seeds are then covered with ether, and shaken with 5% sodium carbonate. The cheirolin is thereby liberated and dissolved by the ether. The ethereal extract is evaporated, and the residue is dissolved in 0.5%

sulphuric acid at 50—60°; the acid solution, after being filtered, is treated with ammonium sulphate, the cheirolin is extracted with ether, and is obtained almost pure by evaporating the ethereal solution after it has been dried with potassium carbonate. The seeds of *Cheiranthus cheiri* yield 1.6—1.7%, and those of *Erysimum arkansanum*, 1.3%.

Cheirolin,  $C_8H_9O_2NS_2$ , m. p. 47—48°, b. p. 200°/3 mm., separates from ether in large, colourless, odourless, prismatic plates,  $a:b:c = 0.9418:1:0.6228$ . Wagner (*loc. cit.*) described it as an alkaloid, but it is entirely without basic properties. The two atoms of sulphur have different functions in the molecule, one being easily oxidised to sulphuric acid, the other only with difficulty. The decomposition of cheirolin by warm dilute acids or alkalis is that of a thiocarbimide, hydrogen sulphide, carbon dioxide, and a primary base,  $C_4H_{11}O_2NS$ , being obtained quantitatively. This supposition is confirmed, not only by the formation of thiocarbamides with ammonia and amines, but also by the production of the same thiocarbamide from cheirolin and aniline, and from phenylthiocarbimide and the base,  $C_4H_{11}O_2NS$ ; by desulphurisation with mercuric oxide, this thiocarbamide yields a carbamide identical with Wagner's cheirol. The base,  $C_4H_{11}O_2NS$ , does not contain hydroxyl; the presence of a sulphone group is indicated by the firmness with which the sulphur is bound, the saturated character and insolubility in ether of the base, its stability to hydrochloric acid at 200°, hydriodic acid, and cold potassium permanganate. Boiling potassium permanganate converts the base into an acid,  $C_8H_9O_2S \cdot CO_2H$ , and fuming nitric acid at 200° produces a good yield of methylsulphonic acid; these two reactions indicate the presence of  $\cdot CH_2 \cdot NH_2$  and of  $\cdot SMe$  respectively. Consequently, the base is probably



and cheirolin a methylsulphone derivative of propylthiocarbimide,  $SO_2Me \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NCS$ , the methylsulphone group being in the  $\gamma$ -position because the substance is optically inactive. The correctness of these views has been proved synthetically. *Methyl- $\gamma$ -bromopropylsulphone*,  $SO_2Me \cdot CH_2 \cdot CH_2 \cdot CH_2Br$ , m. p. 34°, b. p. 156—158°/1 mm., obtained by treating an alcoholic solution of sodium methylmercaptide at 0° with an alcoholic solution of  $\alpha\gamma$ -dibromopropane and oxidising the resulting sulphide with potassium permanganate, is converted by potassium thiocyanate into the *thiocyanate*,



m. p. 57°, but all attempts to convert it into the isomeric thiocarbimide have been unsuccessful. The synthesis of cheirolin has been achieved therefore by the following process. *Methyl*

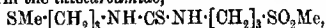
*$\gamma$ -phthaliminopropyl sulphide*,  $C_8H_8 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} N \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot SMe$ , m. p.

59—60°, obtained from alcoholic sodium methylmercaptide and  $\gamma$ -bromopropylphthalimide, yields by hydrolysis *methyl  $\gamma$ -aminopropyl sulphide*, b. p. 170° (*hydrochloride*, m. p. 136°; *oxalate*, decomp. 208°; *picrate*, m. p. 126—127°; *picrolonate*, m. p. 184—185°), the hydrochloride of which is oxidised, best by permanganic acid, to *methyl  $\gamma$ -aminopropylsulphone*, the derivatives of which are identical with those of the primary base obtained by the hydrolysis of cheirolin; for

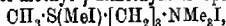


example, the *hydrochloride*, m. p.  $146^{\circ}$ , *platinichloride*, decomposing at  $234^{\circ}$ , *di- $\gamma$ -methylsulphonepropylthiocarbamide*, m. p.  $125-126^{\circ}$ . The synthetic methyl  $\gamma$ -aminopropylsulphone is finally converted into cheirolin by Hofmann's method with carbon disulphide.

The following compounds have also been prepared: Methyl  $\gamma$ -aminopropylsulphone forms, in addition to the derivatives mentioned above, a *picrate*, m. p.  $190-192^{\circ}$ , *picrolonate*, m. p.  $216^{\circ}$ , an *N-benzoyl* derivative, m. p.  $102^{\circ}$ , is oxidised by boiling potassium permanganate to *methylsulphonepropionic acid*,  $\text{SO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $105^{\circ}$ , and is converted by an excess of methyl iodide into *trimethyl- $\gamma$ -methylsulphonepropylammonium iodide*,  $\text{SO}_2\text{Me}\cdot[\text{CH}_2]_3\cdot\text{NMe}_3\text{I}$ , m. p.  $150-152^{\circ}$ . Methyl  $\gamma$ -aminopropyl sulphide reacts with an alcoholic solution of cheirolin to form the *thiocarbamide*,

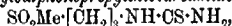


m. p.  $59^{\circ}$ , with alcoholic carbon disulphide to form ultimately *di- $\gamma$ -methylthiopropylthiocarbamide*,  $\text{CS}[\text{NH}(\text{CH}_2)_3\cdot\text{SMe}]_2$ , m. p.  $55-56^{\circ}$ , and with sodium methoxide and an excess of methyl iodide to form the *NS-dimethiodide* of methyl  $\gamma$ -dimethylaminopropylsulphide,



decomposing at  $246^{\circ}$ , and also the *N-methiodide*, decomposing at  $217^{\circ}$ .

An alcoholic solution of cheirolin is converted by alcoholic ammonia into  *$\gamma$ -methylsulphonepropylthiocarbamide*,



m. p.  $116^{\circ}$ , by alcoholic aniline into  *$\gamma$ -methylsulphonepropylphenylthiocarbamide*,  $\text{SO}_2\text{Me}\cdot[\text{CH}_2]_3\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$ , m. p.  $136^{\circ}$  (which is also obtained from phenylthiocarbimide and methyl  $\gamma$ -aminopropylsulphone), and by alcoholic methyl  $\gamma$ -aminopropylsulphone into *s-di- $\gamma$ -methylsulphonepropylthiocarbamide*,  $\text{CS}(\text{NH}\cdot[\text{CH}_2]_3\cdot\text{SO}_2\text{Me})_2$ , m. p.  $125-126^{\circ}$ , which is also obtained by desulphurising an aqueous solution of cheirolin at  $50-60^{\circ}$  with mercuric oxide ( $\frac{1}{2}$  mol.). *s-Di- $\gamma$ -methylsulphonepropylthiocarbamide*, m. p.  $172^{\circ}$ , is obtained by the action of mercuric oxide on the preceding thiocarbamide, or of an excess of mercuric oxide on a boiling aqueous solution of cheirolin. C. S.

**Effect of Pressure and Temperature on Cyanogen.** E. BRINER and A. WRÓCZYŃSKI (*Compt. rend.*, 1910, 151, 314-316. Compare this vol., ii, 557, 707).—The conversion of cyanogen into paracyanogen, which takes place at about  $310^{\circ}$  under ordinary pressure, can be brought about at lower temperatures by increasing the pressure; thus, at  $220^{\circ}$  and 300 atmospheres, the gas undergoes a diminution in volume of 10%, and then contains 16% of free nitrogen. Polymerisation also occurs in the neighbourhood of the critical temperature and pressure, but probably not with sufficient rapidity to vitiate determinations of these constants. W. O. W.

**Formation of *o*-Nitrotoluene from 2:4-Dinitrotoluene.** MORITZ KOHN (*Monatsh.*, 1910, 31, 745-746. Compare Abstr., 1909, i, 561).—*o*-Nitrotoluene is formed by boiling 2:4-dinitrotoluene with an aqueous alkaline solution of hydroxylamine. No trace of the formation of *p*-nitrotoluene could be detected. E. F. A.

**Dinitro-*p*-xylenes.** JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 727—730).—Preparation of the three isomeric nitro-*p*-xylenes by an indirect method has established the fact that it is possible to separate the pure compounds from the mixture resulting from the nitration of *p*-xylene, although only a small proportion of the 2:3- and 2:5-compounds is obtained.

On reduction with ammonium sulphide, 2:3-dinitro-*p*-xylene yields *p*-xylylene-3-sulphonic acid, probably due to replacement of one nitro-group by SH, followed by intramolecular oxidation and the addition of one molecule of water. A. J. W.

**Higher Homologues of Benzene.** ERLING SCHREINER (*J. pr. Chem.*, 1910, [ii], 82, 292—296).—The following compounds are produced by the Grignard and the Friedel-Craft reactions.  $\beta$ -Chloro- $\beta$ -methylpentane, b. p. 110—113°,  $D_4^{20}$  0.8678,  $n_D^{25}$  1.41476, yields with benzene and aluminium chloride  $\beta$ -phenyl- $\beta$ -methylpentane,  $CM_2Pr \cdot Ph$ , b. p. 205—206°,  $D_4^{20}$  0.8796,  $n_D^{25}$  1.49554.  $\beta$ -Chloro- $\beta\delta$ -dimethylpentane,  $CHMe_2 \cdot CH_2 \cdot CMe_2Cl$ , b. p. 126—127°,  $D_4^{20}$  0.8650,  $n_D^{25}$  1.42015, prepared from the corresponding carbinol, is converted into  $\beta$ -phenyl- $\beta\delta$ -dimethylpentane, b. p. 218°,  $D_4^{17}$  0.8741,  $n_D^{25}$  1.49383.  $\gamma$ -Chloro- $\gamma$ -methylpentane, b. p. 116°,  $D_4^{16}$  0.8893,  $n_D^{25}$  1.42315, yields  $\gamma$ -phenyl- $\gamma$ -methylpentane, b. p. 204—206°,  $D_4^{15}$  0.8773,  $n_D^{25}$  1.49724. Triethylcarbinol forms  $\gamma$ -chloro- $\gamma$ -ethylpentane,  $C_2Et_3Cl$ , b. p. 143—144°,  $D_4^{20}$  0.8644,  $n_D^{25}$  1.43276, which is converted into  $\gamma$ -phenyl- $\gamma$ -ethylpentane, b. p. 220—222°,  $D_4^{20}$  0.8656,  $n_D^{25}$  1.49211. C. S.

**The Ditolylmethane from Formaldehyde and Toluene.** OTTO FISCHER and HANS GROSS (*J. pr. Chem.*, 1910, [ii], 82, 231—237).—The large residue obtained in the preparation of ditolylmethane from methylal or paraformaldehyde and toluene (*Abstr.*, 1909, i, 563) yields  $\beta$ -methylanthracene by further distillation. When the residue is distilled under diminished pressure, it yields a further quantity of ditolylmethane and a mobile, colourless liquid with a feeble, blue fluorescence, h. p. 247—250°/12 mm., which is apparently a polymeride of ditolylmethane. When the condensation of toluene and paraformaldehyde or methylal in the presence of sulphuric acid is performed at -15° to -10°, only a little ditolylmethane is obtained, the chief product being an amorphous powder.

The ditolylmethane obtained by the authors' process (and also that prepared by Weiler's method) must contain a little *op*-ditolylmethane, because it does not solidify in ice and salt, melts at -3°, and yields  $\beta$ -methylanthracene by distillation over pumice in a red-hot tube; the pure *dipara*-substance solidifies in ice and salt, melts at 22—23°, and does not yield  $\beta$ -methylanthracene on distillation.

The dinitroditolylmethane obtained by Weiler by the nitration of ditolylmethane is identical with that prepared from *o*-nitrotoluene, formaldehyde, and concentrated sulphuric acid, and must therefore be 3:3'-dinitro-*di-p*-tolylmethane; by reduction, it yields the corresponding diamino-compound,  $C_{16}H_{18}N_2$ , m. p. 72—74°, which forms a diacetyl derivative, m. p. 264°. C. S.

**Ditolylethane and Ditolylethylene from Paraldehyde and Toluene.** OTTO FISCHER and L. CASTNER (*J. pr. Chem.*, 1910, [ii], 280—288).—Continuing a former research (O. Fischer, this Journ., 1875, 154), the authors show that the best condition for the production of ditolylethane is to add slowly paraldehyde to a vigorously stirred mixture of concentrated sulphuric acid and toluene at  $-20^{\circ}$ , the temperature being kept below  $-15^{\circ}$ ; after three to four hours the temperature is slowly increased to  $0^{\circ}$ , and the mass added to water at  $0^{\circ}$ . When cold toluene is added to a mixture of pure sulphuric acid and paraldehyde at  $-20^{\circ}$ , and after three to four hours the temperature is raised to  $10^{\circ}$  and the mass poured into water, the ditolylethane contains 25—33% of di-*p*-tolylethylene, which is separated by fractional distillation. The di-*p*-tolylethylene and the di-*p*-tolylethane obtained from it by reduction with sodium and alcohol do not yield  $\beta$ -methylanthracene when passed over pumice in a red-hot tube. By bromination in carbon disulphide at  $0^{\circ}$ , di-*p*-tolylethylene yields an unstable additive compound, which loses hydrogen bromide during its purification, *o*-bromodi-*p*-tolylethylene,  $C_{16}H_{14}Br$ , m. p.  $53-54^{\circ}$ , being obtained.

The formation of di-*p*-tolylethylene may be due to the intermediate production of crotonaldehyde, since under the conditions mentioned above this aldehyde, toluene, and sulphuric acid produce the unsaturated hydrocarbon. C. S.

**Action of Iodine on *m*-Toluidine.** HENRY L. WHEELER (*Amer. Chem. J.*, 1910, 44, 126—145).—It has been shown by Wheeler and Liddle (this vol., i, 17, 19) that when *p*-toluidine is treated with iodine, both mono- and di-iodo-derivatives are produced, whilst with *o*-toluidine, the mono-derivative only is obtained. A study has now been made of the behaviour of *m*-toluidine towards iodine, and the 6-iodo-, 4:6-di-iodo-, and 2:4:6-tri-iodo-derivatives have been isolated. It is probable that small quantities of isomeric compounds, such as the 4-iodo- and 2:6-di-iodo-derivatives, are also formed. When *m*-toluidine (1 mol.) is mixed with iodine (two or three atoms) in presence of ether, water, and calcium carbonate, the product consists of mono- and di-iodo-toluidines, together with some of the original base. When the proportion of iodine is increased to four atoms, a mixture of the mono-, di-, and tri-iodo-derivatives is obtained, in which the di-derivative predominates, whilst with six atoms of iodine, tri-iodo-*m*-toluidine and resinous material are produced.

[With CHARLES HOFFMAN].—6-Iodo-*m*-toluidine has m. p.  $37-39^{\circ}$ , instead of  $98-99^{\circ}$  as stated by Artmann (Abstr., 1905, i, 879). 6-Iodo-3-acetylaminobenzoic acid,  $NHAc \cdot C_6H_3I \cdot CO_2H$ , m. p.  $210^{\circ}$ , obtained by the oxidation of 6-iodoaceto-*m*-toluidide with potassium permanganate, forms long, colourless, prismatic needles. An attempt was made to prepare 6-iodo-3-aminobenzoic acid by the hydrolysis of the acetyl derivative, but the acid is very unstable, and could not be isolated. 4:6-Di-iodo-*m*-toluidine,  $NH_2 \cdot C_6H_2I_2$ , m. p.  $73-74^{\circ}$ , crystallises in large, stout, colourless needles; the hydrochloride and sulphate were prepared; the acetyl derivative, m. p.  $213^{\circ}$ , forms long, slender, colourless needles, and is only slightly oxidised by potassium permanganate solution even when heated with it in a sealed tube.

at 200°. 2:4:6-*Tri-iodo-m-toluidine*,  $\text{NH}_2 \cdot \text{C}_6\text{HMeI}_3$ , m. p. 135°, crystallises in long, pale brown, hair-like needles; the *acetyl* derivative has m. p. 265°. By the action of potassium iodide on the diazotisation product of 2:4:6-*tri-iodo-m-toluidine*, 2:3:4:6-*tetraiodotoluene*, m. p. 170°, is produced, which forms long needles.

[With CHARLES A. BRAUTLECHT.]—2:6-*Di-iodo-aceto-m-toluidide*,  $\text{C}_6\text{H}_2\text{MeI}_2 \cdot \text{NHAc}$ , m. p. 171°, obtained by the action of iodine chloride on 2-*iodoaceto-m-toluidide*, forms colourless prisms. On hydrolysis, it is converted into 2:6-*di-iodo-m-toluidine*, m. p. 88°, which crystallises in colourless needles and prisms; the *hydrochloride* was prepared. 2:3:6-*Tri-iodotoluene*, m. p. 80·5°, prepared by the action of potassium iodide on the diazotisation product of 2:6-*di-iodo-m-toluidine*, forms colourless needles.

When a mixture of 6-nitro-*o*-toluidine (1 mol.) and iodine (1 mol.) with ether, water, and calcium carbonate is warmed for several hours, 5-*iodo-6-nitro-o-toluidine*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{MeI} \cdot \text{NH}_2$ , m. p. 85°, is produced, which forms yellow prisms. By the action of potassium iodide on the diazotisation product of this base, 2:5-*di-iodo-6-nitrotoluene*,



m. p. 105°, is obtained, which forms colourless needles, and, on reduction, is converted into 3:6-*di-iodo-o-toluidine*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{MeI}_2$ , m. p. 86°, which crystallises in colourless needles. On treating the diazotisation product of 3:6-*di-iodo-o-toluidine* with potassium iodide, 2:3:6-*tri-iodotoluene* is obtained in a yield of 90%. When 5-*iodo-6-nitro-o-toluidine* is diazotised in dilute sulphuric acid solution and the product is decomposed with sodium hydroxide and distilled with steam, 3-*iodo-2-nitrotoluene*, m. p. 65°, is obtained, which forms colourless, prismatic plates.

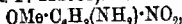
[With SAMUEL R. SCHOLES.]—When 4-*iodo-3-nitrotoluene* is reduced with ferrous sulphate and ammonia, 4-*iodo-m-toluidine* is produced, which has m. p. 38—38·5°, and not 48° as stated by Willgerodt and Simonis (Abstr., 1906, i, 156); the *phenylthiocarbamide* derivative,  $\text{C}_6\text{H}_2\text{MeI} \cdot \text{NH} \cdot \text{CS} \cdot \text{NHPh}$ , has m. p. 162°—163°. 4-*Iodoaceto-m-toluidide* has m. p. 151°, instead of 145—146° as given by Willgerodt and Simonis (*loc. cit.*), and is converted by iodine chloride into 4:6-*di-iodoaceto-m-toluidide*. By the action of iodine on 4-*iodo-m-toluidine*, 4:6-*di-iodo-m-toluidine* is produced. 3:4:6-*Tri-iodotoluene*, m. p. 119—120°, obtained by diazotising 4:6-*di-iodo-m-toluidine* and treating the product with potassium iodide, forms long, slender, brown needles.

When 3-nitro-*p*-toluidine is warmed with iodine chloride and glacial acetic acid, 5-*iodo-3-nitro-p-toluidine*, m. p. 98°, is obtained, which crystallises in golden-brown needles, and yields an *acetyl* derivative, m. p. 202—203°, identical with that obtained by Wheeler and Liddle (this vol., i, 18) by the action of nitric acid on 3-*iodoaceto-p-toluidide*. By diazotising 5-*iodo-3-nitro-p-toluidine* and treating the product with potassium iodide, 4:5-*di-iodo-3-nitrotoluene*, m. p. 84—85°, is produced, which forms rectangular, orange prisms, and on reduction is converted into 4:5-*di-iodo-m-toluidine*, m. p. 66—67°, which forms a mass of colourless, slender needles, and yields an *acetyl* derivative, m. p. 183—184°.

5-Iodo-3-nitrotoluene, m. p. 77°, obtained by the action of potassium iodide on the diazotisation product of 5-nitro-*m*-toluidine, forms yellow, rectangular prisms. On reduction, it is converted into 5-iodo-*m*-toluidine, m. p. 78—78.5°, which crystallises in long, colourless needles; the *acetyl* derivative has m. p. 183°.

E. G.

[Preparation of 5-Nitro-*m*-anisidine.] FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 222062).—5-Nitro-*m*-anisidine,



orange-yellow needles, m. p. 120°, is prepared by the reduction of 3:5-dinitroanisole, m. p. 105°; the 3-nitroanisole 5-*azo-β*-naphthol obtained when it is diazotised and coupled with *β*-naphthol can be employed for the preparation of lakes.

F. M. G. M.

Condensation of Some Primary Aromatic Amines with Chloralaliline. STROUD JORDAN (*J. Amer. Chem. Soc.*, 1910, 32, 973—977).—It is well known that when an amine (1 mol.) is treated with an aldehyde (1 mol.) an additive compound is produced, whilst if the reagents are in the proportion of 2 mols. of the amine to 1 mol. of the aldehyde, a condensation product is formed and water (1 mol.) is eliminated. The experiments now described show that, in certain cases, the additive compound is an intermediate step in the formation of the condensation product, and that it can be converted into the latter on the addition of an excess of free amine.

When an alcoholic solution of freshly prepared chloralaliline is heated with aniline, the condensation product,  $\text{CCl}_3 \cdot \text{CH}(\text{NHPh})_2$ , is obtained.

If chloralaliline is heated with 3-nitro-*p*-toluidine dissolved in benzene, a condensation product,  $\text{CCl}_3 \cdot \text{CH}(\text{NHPh}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{Me} \cdot \text{NO}_2$ , m. p. 98—99°, is obtained, which forms a yellow, crystalline mass, and is difficult to purify owing to the facility with which it decomposes with production of 5-chloro-3-nitro-*p*-toluidine.

E. G.

Preparation of Optically Active *o*-Dihydroxyphenylalkylamines. FARBERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.P. 222451. Compare this vol., i, 372).—It is found that the synthetic optically inactive racemic *o*-dihydroxyphenylalkylamines can be resolved by means of optically active tartaric acids; by this method, *l*-β-3:4-trihydroxyphenylethylmethylamine, identical with the therapeutically important base, *l*-adrenaline, has been obtained. Racemic β-3:4-trihydroxyphenylethylmethylamine (50 parts) is treated with *d*-tartaric acid (43 parts) in either aqueous or alcoholic solution, the solvent removed under reduced pressure, and the residue dried; it is then stirred with methyl alcohol in which *l*-trihydroxyphenylethylmethylamine *d*-tartrate is insoluble, this is crystallised from a mixture of methyl and ethyl alcohols (when pure it has m. p. 149°), and on treatment with alkali yields *l*-adrenaline, m. p. 211—212°. The methyl-alcoholic extract yields the more soluble *d*-trihydroxyphenylethylmethylamine. If *l*-tartaric acid is employed, the *d*-base *l*-tartrate is obtained as the most insoluble component of the mixture. Other racemic dihydroxyphenylalkylamines can be similarly resolved into their active components.

F. M. G. M.

**Unsymmetrical Aromatic Derivatives of Oxamide.**  
 H. SUDA, jun. (*Monatsh.*, 1910, 31, 583—618).—A number of unsymmetrical disubstituted oxamides of the type of phenyltolylloxamide have been prepared by the action of arylamines on ethyl oxanilate and ethyl *p*-tolylloxamate at about 150—200°. The products, with the exception of those which contain para-substituents in both benzene nuclei, give Tafel's reaction with dichromate and concentrated sulphuric acid (Abstr., 1892, 709). The products of hydrolysis of most of the compounds have been examined (compare Dyer and Mixter, Abstr., 1887, 251). Phenyl-*p*-tolylloxamide has m. p. 204—205° (compare Heller, Abstr., 1904, i, 730). Phenyl-*o*-tolylloxamide,  
 $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ ,

crystallises in microscopic prisms, m. p. 176—177°, and is rather more readily soluble than the para-compound. Phenyl-*m*-tolylloxamide crystallises from 60% alcohol in long, colourless, glistening needles, m. p. 168°. All three compounds when boiled with aqueous alcoholic potassium hydroxide yield a mixture of oxanilic and a tolyloxamic acid. With moderately dilute alkali and boiling for about two hours, oxalic acid does not appear to be formed.

Phenyl-*p*-xylyloxamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$  [ $\text{Me}_2:\text{NH} = 1:4:2$ ], forms microscopic needles, m. p. 196—197°; the isomeric *meta*-compound [ $\text{Me}_2:\text{NH} = 1:3:4$ ] has m. p. 200—202°.

Phenyl-*ψ*-cumyloxamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Me}_3$ , has m. p. 202—203° when crystallised from alcohol, but 215—217° when crystallised from acetone. *p*-Tolyl-*p*-xylyloxamide,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}_2$ , crystallises from a mixture of benzene and alcohol in colourless needles, m. p. 168°. Phenyl-*α*-naphthylloxamide,  
 $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ ,

crystallises from alcohol in prismatic needles, m. p. 191—192°, and the isomeric *β*-naphthyl derivative forms a crystalline powder from benzene and has m. p. 227—238°. Phenyl-*p*-nitrophenylloxamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{NO}_2$ , crystallises from ethyl acetate in yellowish-grey needles, m. p. 251—252°. Phenyl-*o*-nitro-*p*-tolylloxamide,  $\text{NHPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NO}_2$  [ $\text{Me}:\text{NO}_2:\text{NH} = 1:3:4$ ], crystallises from alcohol in glistening, golden-yellow plates, m. p. 188—190°.

When phenyl-*p*-tolylloxamide is heated on the water-bath for fifteen minutes with nitric acid (D 1.4), it yields the *o*-mononitro-derivative, m. p. 182—183° and soluble in ethyl acetate, together with the 4:2-dinitro-compound,  $\text{C}_{15}\text{H}_{12}\text{O}_6\text{N}_4$ , insoluble in ethyl acetate, but crystallising from chloroform in yellow, glistening needles resembling pyrites. The constitution of the two nitro-derivatives was established by an examination of the products of hydrolysis; in the case of the dinitro-compound these were oxalic acid, *p*-nitroaniline, and 3-nitro-*p*-toluidine.

Nitric acid and iodine transform phenyl-*p*-tolylloxamide into the *p*-iodo-derivative,  $\text{C}_6\text{H}_4\text{I}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}$ ; this crystallises in microscopic prisms, which are still solid at 280°.

Most of the diarylated oxamides when hydrolysed with dilute alcoholic potassium hydroxide yield an oxamic acid and arylamine; the hydrolysis does not, as a rule, proceed to the formation of oxalic acid. In most cases both the reactions  $\text{NHR}\cdot\text{CO}\cdot\text{CO}\cdot\text{NHR}' + \text{H}_2\text{O} \rightarrow$

$\text{NHR}\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{NH}_2\text{R}'$  and  $\text{NHR}\cdot\text{CO}\cdot\text{CO}\cdot\text{NHR}' + \text{H}_2\text{O} \rightarrow \text{NH}_2\text{R} + \text{CO}_2\text{H}\cdot\text{CO}\cdot\text{NHR}'$  proceed at the same time, so that the final product consists of a mixture of the two substituted oxamic acids and of the two amines. The formation of the two acids was proved by preparing and analysing a mixture of the silver salts of the two acids. In the case of the  $\beta$ -naphthyl, *o*-nitro-*p*-tolyl, and *p*-nitrophenyl derivatives of oxanilide, only one acid is formed, namely, oxanilic. J. J. S.

**Alkylation of Aromatic Amino-acids. III. Aminomethylbenzoic Acids.** HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1910, 44, 113—126).—It has been shown in an earlier paper (this vol., i, 381) that when the salts of *o*-, *m*-, and *p*-aminobenzoic acids are treated with alkyl halides, alkylaminobenzoic acids are produced, but that certain amino-acids which have negative atoms or groups adjacent to the amino-group yield esters under these conditions. It was therefore considered of interest to ascertain whether a similar influence is exerted by substituents which are not usually regarded as having a negative character, such as the methyl group. A study has therefore been made of the ethylation of 4-amino- and 2-amino-mesitylenic acids, and it has been found that the former yields an ester, whilst the latter yields the diethylamino-acid (30 parts), the ethylamino-derivative (10 parts), and the ester (1 part). The investigation has been extended to the ethylation of 4-amino-*m*-toluic acid and 5-iodo-4-amino-*m*-toluic acid. The former gives the ethylamino-derivative (15 parts), the diethylamino-derivative (1 part), and a small quantity of another substance, probably the ester (2 parts). 5-Iodo-4-amino-*m*-toluic acid does not readily undergo alkylation; it yields the ester (15 parts) and the diethylamino-acid (4 parts). These results show that the different behaviour of amino-acids cannot be fully explained either by the theory of stereochemical interference or by the positive or negative character of the substituents.

*Ethyl 4-aminomesitylenate*, m. p. 67°, crystallises in colourless plates.

*2-Diethylaminomesitylenic acid*, m. p. 98°, forms colourless, prismatic crystals, and gives a sky-blue fluorescence in solution in light petroleum. *2-Ethylaminomesitylenic acid*, m. p. 190° (decomp.), crystallises in large, colourless prisms.

4-Nitro-*m*-toluic acid was prepared by the nitration of *m*-toluic acid. An isomeric acid is simultaneously produced, which has been found to be 6-nitro-*m*-toluic acid. The acid obtained by Jacobsen (*Abstr.*, 1882, 185) in this reaction, and supposed to be the 4-nitro-derivative, was doubtless a mixture, as was also the amino-product obtained on reduction. 6-Nitro-*m*-toluamide, m. p. 190°, forms large, transparent prisms. 4-Ethylamino-*m*-toluic acid, m. p. 71—72°, crystallises in large, transparent prisms, and dissolves in light petroleum to form a solution with a sky-blue fluorescence. 4-Diethylamino-*m*-toluic acid, m. p. 55—57°, forms long, slender needles.

5-Iodo-4-amino-*m*-toluic acid, m. p. 212° (decomp.), crystallises in square plates. The ethyl ester, m. p. 70—71°, forms long, colourless

prisms. 5-Iodo-4-diethylamino-m-toluic acid, m. p. 125—126°, forms fine, hair-like crystals. E. G.

**Preparation of Carbamino-acid Esters from 6-Amino- $\alpha$ -naphthol-3-sulphonic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 221967).—The carbamino-acid alkyl or alkylaryl esters of 6-amino- $\alpha$ -naphthol-3-sulphonic acid (J acid) of the general formula  $\text{SO}_3\text{H}\cdot\text{C}_{10}\text{H}_7(\text{OH})\cdot\text{NH}\cdot\text{CO}_2\text{R}$  (R=alkyl or alkylaryl group) can be readily prepared by slowly dropping the required alkyl chlorocarbonate into an aqueous solution of the sodium salt of the above acid at the ordinary temperature and with continual stirring.

Sodium 6-ethylcarbamino- $\alpha$ -naphthol-3-sulphonate is readily soluble in water, the barium salt sparingly so.

Sodium 6-amylicarbamino- $\alpha$ -naphthol-3-sulphonate is sparingly soluble in water, and the solution readily gelatinises.

Sodium 6-benzylcarbamino- and 6-nitrobenzylcarbamino- $\alpha$ -naphthol-3-sulphonates are sparingly soluble in water. F. M. G. M.

**Acyl Derivatives of Thioamides.** MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyōto*, 1909—1910, 2, 241—244).—Thiobenzamide and thio-*p*-toluamide when dissolved in benzene react with acid chlorides with the formation of nitrogen-substituted compounds of the constitution  $\text{R}\cdot\text{CS}\cdot\text{N}(\text{OCR}')_2$  or  $\text{R}\cdot\text{CS}\cdot\text{N}\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\rangle\text{R}''$ . The reaction takes place at the ordinary temperature, occasional cooling being necessary. The resulting compounds are stable towards hydrochloric acid, but easily decomposed by alkalis or by reducing agents, hydrogen sulphide being one of the decomposition products in both cases.

Phthalylthiobenzamide,  $\text{C}_6\text{H}_5\cdot\text{CS}\cdot\text{N}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_4$ , crystallises from benzene in stout violet plates containing half a molecule of benzene of crystallisation. From alcohol, it crystallises in scales, and from ether in prisms, and has m. p. 126°. Phthalylthio-*p*-toluamide,

$\text{C}_6\text{H}_7\cdot\text{CS}\cdot\text{N}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_4$ , forms violet scales or needles, m. p. 179°. Succinylthio-*p*-toluamide,  $\text{C}_7\text{H}_7\cdot\text{CS}\cdot\text{N}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_4$ , forms violet, needle-shaped crystals, m. p. 142°. Acetylthiobenzamide,  $\text{Ph}\cdot\text{CS}\cdot\text{N}\cdot\text{Ac}$ , forms red plates, m. p. 94—95°. Acetylthio-*p*-toluamide,  $\text{C}_7\text{H}_7\cdot\text{CS}\cdot\text{N}\cdot\text{Ac}$ , crystallises in red plates, m. p. 121—123°. T. S. P.

**Diguaiacylphosphoric Acid.** PIERRE DUFUIS (*Bull. Soc. chim.*, 1910, [iv], 7, 846—847. Compare *Abstr.*, 1908, i, 529; this vol., i, 248).—On adding phosphoric anhydride to guaiacol and heating to 110°, a mixture of mono- and diguaiacylphosphoric acids is formed, from which the former may be separated by neutralisation with sodium carbonate solution and precipitation with copper sulphate. From the filtrate, diguaiacylphosphoric acid separates on adding hydrochloric acid, and can be recrystallised from boiling water. The potassium salt is isomorphous with the sodium salt (*loc. cit.*), and crystallises with 1 mol.  $\text{H}_2\text{O}$ . T. A. H.

**Preparation of Hexa- and Penta-methylphloroglucinol.** JOSEF HERZIG and BR. ERTHAL (*Monatsh.*, 1910, 31, 827—831).—The



methylation in the nucleus of phloroglucinol and orcinol (Herzig and Wenzel, *Abstr.*, 1906, i, 93) is a complicated reaction, and the yield is dependent on factors which are still imperfectly understood.

Hexamethylphloroglucinol could not be prepared by Spitzer's method (*Abstr.*, 1890, 1110), but both hexa- and penta-methyl derivatives are obtained on warming phloroglucinol in aqueous alkaline solution with methyl iodide until the reaction is neutral. The hexa-methyl derivative crystallises out, and the pentamethyl derivative is extracted from the residue with ether. The yield is satisfactory, but the relative proportions of the two products vary in the different experiments. The pentamethyl derivative can be further methylated to hexamethylphloroglucinol by the same treatment in aqueous solution, a transformation which does not take place in alcohol.

Pentamethylphloroglucinol is converted by the action of diazo-methane into the methyl ether, m. p. 52–55°, which was previously known as a viscid oil obtained by the action of methyl iodide and potassium hydroxide.

E. F. A.

Some Cyclic Ethylenic Ethers and their Bromo derivatives. G. BUSIGNIES (*Compt. rend.*, 1910, 151, 515–517).—The Grignard reaction proceeds much more readily with substituted alkoxy-aromatic ketones than with the alkylamino-ketones studied previously (*Abstr.*, 1909, i, 736). Phenyl phenetidyl ketone yields in this way phenyl-*p*-phenetidylethylene, m. p. 71°, phenyl-*p*-phenetidylpropylene m. p. 54°, and *p*-phenetidylstilbene, m. p. 93°.

The bromination of phenyl-*p*-anisylethylene has been studied, but the author has been unable to obtain the isomeric monobromo-derivatives described by Stoermer and Simon (*Abstr.*, 1905, i, 53). Compounds of this class containing the grouping  $\text{CH}_2\text{:C}$  yield only dibromo-derivatives even in the cold, whilst those containing the grouping  $\text{CH:C}$  furnish monobromo-derivatives with liberation of hydrogen bromide. Phenyl-*p*-anisylethylene gives a dibromo-derivative,  $\text{C}_{15}\text{H}_{14}\text{OBr}_2$ , m. p. 115°; the corresponding compound from phenyl-*p*-phenetidylethylene has m. p. 90°.  $\beta$ -Bromo- $\alpha$ -phenyl-*p*-phenetidylpropylene has m. p. 48°.  $\beta$ -Bromo- $\alpha$ -*p*-phenetidylstilbene, m. p. 73° forms a dibromo-derivative,  $\text{C}_{22}\text{H}_{18}\text{OBr}_2$ , m. p. 150°.  $\beta$ -Bromodiphenetidylpropylene has m. p. 60°.

W. O. W.

Catalytic Preparation of Mixed Ethers from Alcohols and Phenols. PAUL SARATIE and ALPHONSE MAILHE (*Compt. rend.* 1910, 151, 359–362. Compare this vol., i, 294, 456, 536).—Phenol (1 vol.) and methyl alcohol (1.5 vols.) in the state of vapour are passed over a column of thorium oxide at 390–420°. The product are fractionated, and the middle portion washed with sodium hydroxide solution. Anisole is thus obtained in excellent yield after a single rectification. Under the same conditions, *m*-cresol gives very good yield of the methyl ether, but with the para-compound the yield is less satisfactory. The method is successful with 2:4-xylene thymol, carvacrol,  $\beta$ -naphthol, and  $\alpha$ -naphthol. In the latter case the catalyst is kept at about 400°, and the yield is 33%.

Ethers were not obtained from dihydric phenols owing to the

formation of stable compounds with the thorium oxide, these being slowly decomposed with formation of complex products.

The homologues of anisole are obtained with less ease owing to the readiness with which the higher alcohols undergo dehydration. The reaction, however, offers an advantageous means of preparation if the phenol is dissolved in excess of the alcohol. The ethyl, propyl, and amyl ethers of phenol, and *p*-tolyl ethyl ether were prepared in this way.

W. O. W.

#### Catalytic Preparation of Phenyl and Diphenyl Ethers.

PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1910, 151, 492—494. Compare preceding abstract).—Diphenyl oxide and its homologues are readily prepared by passing the vapour of a phenol over thorium oxide at 390—450°. Solid phenols may be dissolved in benzene before vaporisation. The catalytic method gives a yield of 50% of the oxide in the case of phenol and *p*- and *m*-cresol. With *o*-cresol, however, a higher temperature is necessary and the yield is poor.

When the reaction is allowed to proceed at a higher temperature, hydrogen is liberated and a diphenylene oxide produced. In the case of phenol and *p*-cresol, considerable quantities of the condensed oxides are formed at 475°; *m*-cresol under these conditions gives rise to *m*-ditolylene oxide,  $C_{14}H_{14}O$ , brilliant lamellae, m. p. 182°. The analogous *ortho*-compound has m. p. 121°.

W. O. W.

Scission of Phenolic Ethers by Organo-magnesium Compounds. VICTOR GRIGNARD\* (*Compt. rend.*, 1910, 151, 322—325. Compare Abstr., 1904, i, 494).—Organo-magnesium derivatives do not react with phenolic ethers under ordinary conditions. By adding magnesium, however, to a mixture of an alkyl bromide with anisole or phenetole in equimolecular proportions, employing benzene as the solvent, reaction occurs. Hydrolysis of the product in the usual way regenerates the phenolic ether, but if the solvent is removed and the residue gradually heated to 150—160° under 10—15 mm., only half the ether is recovered, the remainder having undergone conversion into phenol. Under the same conditions, estragole gave a 50% yield of *p*-allylphenol. In the case of safrole, fission takes place at the temperature of the water-bath, but the unstable dihydroxy-derivative cannot be isolated. A small quantity of a substance, probably 2-methoxy-5-allylphenol, is also produced.

The foregoing results are explained by supposing that an oxonium complex is first produced by addition, and that this undergoes scission, yielding the compound  $OPh \cdot MgBr$ , and probably ethylene and a saturated hydrocarbon.

The results obtained by Schorigin by the action of alkyl derivatives of sodium with ethers may be explained in the same way (this vol., i, 547).

W. O. W.

Action of Bromine in Presence of Aluminium Bromide on Phenyl Ethers. A. BONNEAUD (*Bull. Soc. chim.*, 1910, [iv], 7, 776—781).—Bodroux has shown (Abstr., 1898, i, 641) that in the case of phenols, bromine in excess in presence of aluminium bromide

(1) displaces all the hydrogen atoms in the nucleus; (2) leaves unchanged lateral chains of the type  $\cdot\text{CH}_2\text{R}$ , and (3) destroys lateral chains attached to the nucleus by  $\cdot\text{CH}$  or  $\cdot\text{C}$ , replacing each of these by one atom of bromine. The author shows that the same rules hold good in the case of phenyl alkyl ethers, and that in addition these ethers undergo saponification and regenerate the corresponding phenols, except in the case of ethers containing two aromatic nuclei; thus, under these conditions, anisole, phenetole, and phenyl propyl ether all yield pentabromophenol, diphenyl ether furnishes *decabromodiphenyl ether*, colourless prisms, m. p.  $293^\circ$ , whilst the methyl and ethyl ethers of *o*-, *m*-, and *p*-cresols and the methyl and ethyl ethers of thymol and carvacrol all give the corresponding tetrabromocresols. The following new compounds were prepared by the action of the appropriate alkyl iodide on the potassium derivative of pentabromophenol, *pentabromo-anisole*, m. p.  $174^\circ$ , *pentabromophenetole*, m. p.  $136^\circ$ , and *pentabromophenyl propyl ether*, m. p.  $98^\circ$ .

T. A. H.

**The Cholesterol Group. VIII. isoCholesterol.** A. MORESCHI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 53—57. Compare this vol., i, 317, and Darwüädter and Lifschütz, Abstr., 1898, i, 245).—Along with coprosterol and hippocoprosterol (Dorée and Gardner, Trans., 1908, 1625; Abstr., 1908, ii, 514), *isocholesterol* belongs to the group of the hydrosterols. To obtain it, wool fat is repeatedly extracted with boiling alcohol, the residue is subjected to saponification, and the unsaponified portion is fused for some hours in contact with an excess of benzoic anhydride. The mixture of cholesteryl benzoate and *isocholesteryl benzoate* obtained is purified by means of boiling alcohol, and by precipitation from ether with alcohol. The separation of the two substances can be effected by recrystallisation from a mixture of benzene and ether. *isocholesteryl benzoate* forms small needles, m. p.  $199^\circ$ ,  $[\alpha]_D^{20} + 73.33^\circ$ . It is saponified by alcoholic potassium hydroxide, yielding *isocholesterol*, which crystallises in long, slender needles, m. p.  $140$ — $141^\circ$ . The quantity formed in the saponification agrees with the formula  $\text{C}_{27}\text{H}_{45}\cdot\text{OBz}$ . The molecular weight of *isocholesterol* (in naphthalene) was found to be  $372$ — $378^\circ$ , agreeing with that required by the formula  $\text{C}_{27}\text{H}_{45}\cdot\text{OH}$ . The substance has  $[\alpha]_D^{20} + 59.1^\circ$ . In ethereal solution in presence of platinum black, it is not acted on by hydrogen. The *formate* has m. p.  $108$ — $110^\circ$ ;  $[\alpha]_D^{20} + 46.47^\circ$ . By the action of bromine on *isocholesterol*, a *bromo-derivative* is obtained.

R. V. S.

**Nitration of Hemipinic Acid and its Esters.** RUDOLF WEGSCHEIDER and ALFONS KLEMMENC (*Monatsh.*, 1910, 31, 709—743).—On energetic nitration of  $\alpha$ -methyl hemipinate, Wegscheider and Strauch (Abstr., 1908, i, 794) obtained methyl dinitrodimethoxybenzoate, and Wegscheider and Müller (Abstr., 1908, i, 896) prepared the same compound from methyl opianate; it is therefore regarded as a derivative of 2:3-dimethoxybenzoic acid, a conclusion based on the supposition that no wandering takes place of the methyl attached to the carbonyl group during nitration. This is confirmed by the behaviour of  $\beta$ -methyl hemipinate, which yields a derivative of protocatechuic acid.

Hemipinic acid yields on nitration nitrohemipinic acid and small quantities of 6-nitro-2:3-dimethoxybenzoic acid; energetic nitration converts either of these or hemipinic acid itself directly into 5:6-dinitro-2:3-dimethoxybenzoic acid.  $\alpha$ -Methyl hemipinate forms the methyl ester of this acid, whereas  $\beta$ -methyl hemipinate forms methyl-2:6-dinitroveratrate. Lastly, dimethyl hemipinate forms dimethyl-5:6-dinitrohemipinate. In every instance on energetic nitration the esterified carboxyl group remains untouched; the unprotected carbonyl, however, is eliminated and its position occupied by a nitro-group when the second nitro-group is introduced. Apparently, methoxyl groups have a greater influence than carboxyl groups on the position occupied by the new substituting substance.

The proof of the constitution of 6-nitro-2:3-dimethoxybenzoic acid depends on (1) the formation from hemipinic acid, (2) the fact that it differs from the three possible nitroveratric acids, (3) the fact that it cannot be esterified by methyl alcohol and hydrogen chloride, (4) that it is convertible into 4-nitrocatechol. The constitution of 5:6-dinitro-2:3-dimethoxybenzoic acid is established by the fact that the isomeric methyl hemipinates give isomeric dinitro-derivatives; the position 6 for one nitro-group is fixed by the formation of this acid from 6-nitro-2:3-dimethoxybenzoic acid, and the position 5 for the other nitro-group is established by the formation from nitrohemipinic acid.

*Meth.*, 2:6-dinitro-3:4-dimethoxybenzoate, prepared by nitration of  $\beta$ -methyl hemipinate with fuming nitric acid without a solvent, crystallises in colourless, lustrous, long needles, m. p. 136—136.5°.

2:6-Dinitroisovanillic acid, prepared by boiling the above compound with dilute potassium hydroxide, separates in well formed crystals, m. p. 206° (decomp.). It gives a brownish-red precipitate with ferric chloride. Crystallographic measurements prove its identity with the acid described by Matthiessen and Foster (*Jahresber.*, 1867, 520) as dinitromethylhypogallic acid. It cannot be esterified by methyl alcohol and hydrogen chloride. The *silver* salt was obtained as a yellow, crystalline, explosive substance; the *disilver* salt is red. The *methyl* ester, prepared by the interaction of methyl iodide and the mono-silver salt, crystallises in long, yellow needles, m. p. 163—164°. The *acetate* forms lustrous plates, m. p. 126—129°.

2:6-Dinitroacetylisovanillic acid, prepared by heating the acid with acetic anhydride, forms a colourless, crystalline mass, m. p. 156° (decomp.).

2:6-Dinitroveratric acid, prepared by hydrolysis of the methyl ester with the calculated amount of aqueous potassium hydroxide crystallises in long, yellow needles, which soften at 191°, m. p. 194—195°. It cannot be acetylated.

Dimethyl 6-nitrohemipinate, prepared by the action of fuming nitric acid on dimethyl hemipinate, has m. p. 83—84° [Wegscheider and Rušnov (*Ahstr.*, 1908, i, 793) found 77—78°]. It crystallises in the triclinic system,  $a:b:c = 1:0.7192:0.6303$ .  $\alpha = 88^\circ 0'$ ,  $\beta = 88^\circ 56'$ ,  $\gamma = 98^\circ 31'$ .

Dimethyl dinitrohemipinate crystallises in slender, colourless needles, m. p. 120—121°. On hydrolysis, *dinitrohemipinic acid*, a colourless,

crystalline powder, m. p. 163° (decomp.), obtained. When heated in a stream of carbon dioxide at the melting point, it is converted into the anhydride, m. p. 113—114°.

6-Nitro-3:3-dimethoxybenzoic acid (Wegscheider and Rušnov, *loc. cit.*) is colourless, m. p. 189—190°, and differs from the three known nitroveratric acids. The methyl ester has m. p. 76—77°. By the action of aniline, 5-nitroguaiacol is formed, which yields 4-nitroveratrole on methylation.

4-Nitroguaiacyl acetate, prepared from nitroguaiacol and acetic anhydride, forms colourless needles, m. p. 108—109°. E. F. A.

Two Aromatic Acids of the Series,  $C_nH_{2n-8}O_8$ . F. BODROUX (*Bull. Soc. chim.*, 1910, [iv], 7, 847—848).— $\alpha$ -Phenyl- $\alpha$ -ethylbutyric acid  $CEt_2Ph \cdot CO_2H$ , obtained with the amide by the hydrolysis of the corresponding nitrile (this vol. i, 482, 557), crystallises from alcohol in small, colourless prisms, m. p. 93°.  $\alpha$ -Phenyl- $\gamma$ -methyl- $\alpha$ -isobutylvaleric acid,  $O(CH_2Pr)_2Ph \cdot CO_2H$ , similarly obtained (this vol. i, 482), crystallises from light petroleum in large, colourless prisms, m. p. 75—76°. T. A. H.

Synthetic Preparation of Esters of  $\alpha\beta$ -Diphenylsuccinic Acid. TELEMACHOS KOMNENOS (*Annalen*, 1910, 375, 254—259).—The reaction between ethereal iodine and an alcoholic solution of ethyl phenylacetate and sodium ethoxide yields ethyl (*b*)- $\alpha\beta$ -diphenylsuccinate, m. p. 140°; the acid, m. p. 160°, obtained by its hydrolysis is probably a mixture of the *a* and *b* forms of  $\alpha\beta$ -diphenylsuccinic acid. Ethereal iodine reacts with a methyl-alcoholic solution of ethyl phenylacetate and sodium methoxide to form methyl (*a*)- $\alpha\beta$ -diphenylsuccinate,  $[CO_2Me \cdot CHPh]_2$ .

m. p. 210°; the acid obtained by its hydrolysis softens at 187°, melts at 223° (decomp.), and forms a barium salt containing  $2H_2O$ , and is, therefore, (*a*)- $\alpha\beta$ -diphenylsuccinic acid. C. S.

Action of Unsaturated Dicarboxylic Acids on *p*-Aminophenole. ARNALDO PIUTTI (*Gazzetta*, 1910, 40, i, 525—568. Compare Abstr., 1908, i, 783; this vol. i, 22, 264).—[With A. PAGNIELLO and A. MARCIANO.]—Citraconic Derivatives.—*p*-Hydroxyphenylcitraconamic acid,  $C_{11}H_{11}O_4N$ , forms yellow, acicular prisms, m. p. 155°. *p*-Methoxyphenylcitraconamic acid,  $C_{12}H_{13}O_4N$ , may be obtained by the method previously given, and also (1) by saponifying *p*-methoxyphenylcitraconimide with alcoholic potassium hydroxide; (2) by acting on *p*-anisidine (in light petroleum) with mesaconylchloride. It crystallises in long, yellow prisms, m. p. 167°, and gives a violet coloration with ferric chloride. *p*-Ethoxyphenylcitraconamic acid,  $C_{13}H_{15}O_4N$ , prepared by the above methods, forms yellow needles, m. p. 162°, and gives a yellow coloration with ferric chloride.

*p*-Hydroxyphenylcitraconimide,  $C_{11}H_9O_3N$ , is a dark yellow, crystalline substance, m. p. 170°. *p*-Methoxyphenylcitraconimide,  $C_{12}H_{11}O_3N$ , forms yellow crystals, m. p. 121°; it gives a violet coloration with alcoholic potassium hydroxide. *p*-Ethoxyphenylcitraconimide,

$C_{13}H_{13}O_3N$ , crystallises in canary-yellow needles, m. p. 109°.

The diamides obtained from citraconic anhydride or citraconyl chloride by the methods already indicated are found to be mesaconic derivatives, identical with those obtained directly from mesaconic acid. The *p*-hydroxyphenyl derivative could not be obtained. *p*-Methoxyphenylmesacondiamide,  $C_{19}H_{20}O_4N_2$ , forms colourless, lustrous scales, m. p. 206°. *p*-Ethoxyphenylmesacondiamide,  $C_{21}H_{24}O_4N_2$ , crystallises similarly, and has m. p. 205°.

[With C. SCHIFANI.]—*Mesaconic Derivatives*.—Mesaconamic acids and mesaconimides could not be prepared, but in their stead corresponding citraconic derivatives appeared. On the other hand, *p*-methoxy- and *p*-ethoxy-phenylmesacondiamides were obtained, identical with those from citraconic acid (*v.g.*).

By the action of mesaconyl chloride on *p*-anisidine in addition to *p*-methoxyphenylcitraconamic acid, a colourless substance, m. p. 235°, was obtained.

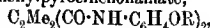
[With IDA FOX and L. ROSSI.]—*Itaconic Derivatives*.—Of the four isomeric *p*-hydroxyphenylitaconamic acids,  $C_{11}H_{11}ON_2$ , which might be expected, only three could be prepared. On mixing equimolecular quantities of itaconic anhydride and *p*-aminophenol, dissolved in benzene and in acetone respectively, one isomeride is precipitated; it forms colourless needles, m. p. 161—162° (forming a yellowish-brown liquid), and gives no coloration with ferric chloride. The *silver* salt was prepared. Another isomeride, a yellow, crystalline powder, m. p. 118—119°, is obtained by dissolving the corresponding imide in sodium hydroxide and precipitating with acid; it gives a red coloration with ferric chloride. When it is boiled with water, it yields the third isomeride, which is colourless, has m. p. 97—98°, and gives no coloration with ferric chloride. By similar methods, three corresponding isomeric *p*-methoxyphenylitaconamic acids,  $C_{12}H_{13}O_4N$ , are obtained. The first forms colourless, acicular crystals, m. p. 166—167° (forming a yellow liquid), and gives no coloration with ferric chloride. The *silver* salt was obtained. The second isomeride is yellow, and has m. p. 144—145°; it yields a red coloration with ferric chloride. The *silver* salt was prepared. The other isomeride is colourless, has m. p. 135—136°, and gives no coloration with ferric chloride. The *silver* salt was prepared. There are three corresponding isomeric *p*-ethoxyphenylitaconamic acids,  $C_{13}H_{15}O_4N$ . The first forms colourless, lustrous scales, m. p. 165—166°, and gives no reaction with ferric chloride. The *silver* salt was prepared. A second isomeride forms a yellow precipitate, m. p. 148—149°, and gives a red coloration with ferric chloride. The *silver* salt was prepared. The third isomeride is a colourless, crystalline substance, m. p. 134—135°. The *silver* salt was also obtained.

The imides corresponding with the above acids were prepared (1) by heating the acids in an atmosphere of carbon dioxide at a temperature a little above their melting points; (2) by heating at 130° in carbon dioxide mixtures of itaconic anhydride with the aminophenols. *p*-Hydroxyphenylitaconimide,  $C_{11}H_9O_3N$ , forms yellow crystals, m. p. 104—105°. *p*-Methoxyphenylitaconimide,  $C_{12}H_{11}O_3N$ , crystallises in small, yellow needles, m. p. 101—103°; it gives an intense, reddish-violet coloration with sodium ethoxide. *p*-Ethoxyphenylitaconimide,

$C_{18}H_{13}O_4N$ , forms yellow needles, m. p. 99—100°, and gives a reddish-violet coloration with potassium or sodium hydroxide.

The itacondiamides were obtained by the method previously described. *p*-Hydroxyphenylitacondiamide,  $C_{17}H_{10}O_4N_2$ , crystallises in small, light brown laminae, m. p. 132—133°. *p*-Methoxyphenylitacondiamide,  $C_{19}H_{12}O_4N_2$ , forms lustrous scales, m. p. 155—156°. *p*-Ethoxyphenylitacondiamide,  $C_{21}H_{14}O_4N_2$ , crystallises similarly, and has m. p. 173—174°.

[With GINO ABATI.]—*Pyrocinchonic Derivatives*.—Of the derivatives of this acid, only the imides could be prepared, in addition to *p*-anisidine *p*-methoxyphenylpyrocinchonamate,



and *p*-phenetidine *p*-ethoxyphenylpyrocinchonamate.

*p*-Hydroxyphenylpyrocinchonimide,  $C_{15}H_{11}O_3N$ , was obtained by (1) heating to boiling point an alcoholic solution of pyrocinchonic anhydride and *p*-aminophenol, a current of sulphur dioxide being afterwards passed to reduce the coloration of the liquid; (2) mixing the two substances in the presence of acetone in the cold, sulphur dioxide being afterwards employed to decolorise the liquid. In the latter case, indications were obtained of the formation and subsequent decomposition of *p*-aminophenol *p*-hydroxyphenylpyrocinchonamate. When the imide is treated with alcoholic potassium hydroxide and then acidified, it separates out unchanged. The imide forms large, canary-yellow crystals, m. p. 200°. When it is precipitated from alcohol with water, or when it is powdered in a mortar, it is obtained in colourless crystals, which have the same m. p. and composition as the other form.

*p*-Anisidine and pyrocinchonic anhydride in alcoholic solution in the warm, and in acetone at the ordinary temperature, yield *p*-methoxyphenylpyrocinchonimide,  $C_{15}H_{13}O_3N$ , crystallising in straw-yellow prisms, m. p. 139°. From some solvents it is obtained in colourless crystals, which become yellow on melting, and remain so on resolidification. *p*-Anisidine and the anhydride react in benzene solution at the ordinary temperature, yielding *p*-anisidine *p*-methoxyphenylpyrocinchonamate,  $C_{20}H_{24}O_3N_2$ , which forms small, white needles, m. p. 90—91° (becoming yellow at about 85°). In solution (in ethylene bromide) the substance decomposes into its three constituents. *p*-Ethoxyphenylpyrocinchonimide,  $C_{17}H_{15}O_3N$ , forms lustrous, yellow needles, m. p. 117°. The colourless form has m. p. 116—117°. *p*-Phenetidine *p*-ethoxyphenylpyrocinchonamate crystallises in minute, colourless needles, which become yellow at 80° and melt at 94° to a yellow liquid, which remains yellow on solidification.

[With C. ALLEGRI.]—*Phthalic, Citraconic, Itaconic, and Maleic Derivatives of o*-Anisidine.—*o*-Methoxyphenylphthalamic acid,



forms colourless crystals, m. p. 168—169°, and gives with ferric chloride a yellow coloration, which becomes reddish-violet. *o*-Methoxyphenylcitraconamic acid,  $C_{15}H_{13}O_5N$ , crystallises in canary-yellow needles, m. p. 116—117°, and yields an intense reddish-violet coloration with ferric chloride. *o*-Methoxyphenylitaconamic acid,  $C_{17}H_{15}O_5N$ , forms small, colourless needles, m. p. 128—129°, and gives a pale

violet coloration with ferric chloride. *o*-Methoxyphenylmaleinamic acid,  $C_{11}H_{11}O_4N$ , an amorphous, yellow powder, has m. p. 144–145°, and gives with ferric chloride a wine-red coloration.

*o*-Methoxyphenylphthalimide,  $C_{15}H_{11}O_4N$ , crystallises in colourless prisms, m. p. 155–156°. *o*-Methoxyphenylcitraconimide,  $C_{12}H_{11}O_5N$ , a pale yellow powder, has m. p. 98–99°, and gives a violet coloration with alcoholic potassium hydroxide. *o*-Methoxyphenylitaconimide,  $C_{12}H_{11}O_5N$ ,

is a colourless powder, m. p. 112–113°. *o*-Methoxyphenylmaleinimide could not be obtained.

[With G. LEONE and C. D'EMILIO.]—*Camphoric Derivatives*.—*α*-*cis*-

*p*-Hydroxyphenylcamphoramic acid,  $\begin{matrix} H \\ | \\ C_7H_{10} \end{matrix} \begin{matrix} CO \cdot NH \cdot C_6H_4 \cdot OH \\ | \\ CO_2H \end{matrix}$ ,

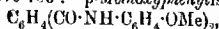
prepared by heating camphoric anhydride and *p*-aminophenol in boiling acetone for half an hour, has m. p. 165° (becoming brown at 155°),  $[a]_D^{16} + 46.36^\circ$ . *α*-*trans*-*p*-Hydroxyphenylcamphoramic acid,

$\begin{matrix} H \\ | \\ C_7H_{10} \end{matrix} \begin{matrix} CO \cdot NH \cdot C_6H_4 \cdot OH \\ | \\ Me \end{matrix}$ , is obtained when an aqueous solu-

tion of the potassium salt of the preceding acid is heated for ten hours in an autoclave at 120°, and then treated with hydrochloric acid; it has m. p. 226°,  $[a]_D^{16} + 13.48^\circ$ . *α*-*p*-Hydroxyphenylcamphoramic acid (I),  $C_{16}H_{21}O_4N$ , from camphoric anhydride and *p*-aminophenol in acetone at the ordinary temperature, becomes brown at 205° and decomposes at 220°. It has  $[a]_D^{16} + 52.4^\circ$ . When heated in alcoholic solution, it is converted into the *α*-*cis*-form, m. p. 165°. A *p*-hydroxyphenylcamphoramic acid (I),  $C_{16}H_{21}O_4N$ , is also obtained by heating camphoric anhydride and *p*-aminophenol in a sealed tube for five hours at 120°. It forms colourless crystals, m. p. 185°,  $[a]_D^{19} + 12.4^\circ$ . A *p*-methoxyphenylcamphoramic acid (I),  $C_{17}H_{23}O_4N$ , is obtained on mixing benzene solutions of camphoric anhydride and *p*-anisidine. It forms large, colourless prisms, m. p. 198°. *α*-*cis*-*p*-Ethoxyphenylcamphoramic acid,  $C_{18}H_{25}O_4N$ , is prepared by heating camphoric anhydride with *p*-phenetidine for two hours, or by heating without a solvent for eight hours in an autoclave. It forms colourless crystals, m. p. 199°,  $[a]_D^{19} + 51.4^\circ$ . *α*-*trans*-*p*-Ethoxyphenylcamphoramic acid is obtained in the same way as the corresponding methoxy-derivative. It has m. p. 184°,  $[a]_D^{19} + 2.81^\circ$ .

*p*-Hydroxyphenylcamphorimide,  $C_{16}H_{19}O_4N$  (from camphoryl chloride and *p*-aminophenol in acetone), has m. p. 218°,  $[a]_D^{23} + 5.49^\circ$ . *p*-Methoxyphenylcamphorimide,  $C_{17}H_{21}O_4N$ , forms colourless crystals, m. p. 110°. *p*-Ethoxyphenylcamphorimide crystallises in colourless needles, m. p. 114°,  $[a]_D^{23} - 13.28^\circ$ .

[With D. PUGLIESE and G. SELVAGGI.]—*isoPhthalic and Terephthalic Derivatives*.—No product of the action of *isophthalic* acid on *p*-aminophenol in boiling alcohol could be isolated. The reactions with *p*-anisidine and *p*-phenetidine respectively, under the same conditions, yielded *p*-anisidine hydrogen phthalate, which on heating becomes brown above 200°, and *p*-phenetidine hydrogen phthalate, which becomes brown on heating above 100°. *p*-Methoxyphenylisophthaldiamide,



was obtained, however, by heating the acid with *p*-anisidine to 280°.

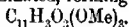


It crystallises in colourless needles, m. p. 268°. *p*-Methoxyphenylterephthaldiamide, similarly obtained by heating to 150°, forms lustrous scales, m. p. 246—248°. *p*-Ethoxyphenylterephthaldiamide, similarly prepared by heating at 180° for two hours, forms grey needles, which, on heating to 300°, become brown, but do not melt. R. V. S.

**Galloflavin. VI. Lactone Dyes.** JOSEF HERZIG [with GEZA ERDŐS and GRETE RUZICKA] (*Monatsh.*, 1910, 31, 799—818. Compare Herzig and Epstein, *Abstr.*, 1908, i, 899).—Galloflavin belongs to quite a different class of substances than resoflavin, which is classed as a derivative of diphenylbimethylole. Galloflavin is completely methylated by diazomethane (Herzig and Tschorne, *Abstr.*, 1904, i, 814). Unlike resoflavin, on further treatment of this methylated derivative with potassium hydroxide and methyl sulphate or methyl iodide, it cannot be converted into the methyl ethyl ester, but yields a mixture of tarry products. A further point of difference is in the behaviour towards potassium hydroxide; methyl galloflavin dissolved in the cold yields on acidification a hydrolysed substance with fewer methoxyl groups, and the latter when methylated gives a substance isomeric with the original. The new compound is provisionally termed *isogalloflavin trimethyl ether*,  $C_{11}H_3O_3(OMe)_3$ , and the new ether is *isogalloflavin tetramethyl ether*,  $C_{12}H_2O_4(OMe)_4$ . Galloflavin, therefore, has the formula  $C_{13}H_2O_4(OH)_4$ , with which this analysis of the acetyl derivative agrees.

The conversion into *isogalloflavin trimethyl ether* gives only about 45% of the theoretical yield, together with a syrupy product.

*iso*Galloflavin trimethyl ether is a pronounced acid; at the melting point carbon dioxide is eliminated, forming the compound,



It contains a lactone ring which is opened by treatment with potassium hydroxide and methyl iodide or sulphate, yielding a crystalline substance. This ether ester is quantitatively hydrolysed to the ether acid,  $C_{11}H_2O(OMe)_4(CO_2H)_2$ , which again loses carbon dioxide at the melting point, forming an acid,  $C_{10}H_3O(OMe)_4 \cdot CO_2H$ . It remains to determine the function of the last oxygen atom, the constitution of the complex,  $C_{10}H_3$  or  $C_{10}H_{10}$ , and the relation of the *iso*-derivative to galloflavin.

Purpurogallin,  $C_{11}H_4O(OH)_4$ , has been shown by A. G. Perkin to undergo an isomerisation with potassium hydroxide similar to galloflavin, and it is possible that the  $C_{10}$  complex is the same in each case.

Tetra-acetylgalloflavin is colourless, m. p. 230—233°. Galloflavin tetramethyl ether forms colourless, matted needles, m. p. 236—239°. *iso*Galloflavin trimethyl ether forms colourless needles, m. p. 253—256° (decomp.). *iso*Galloflavin tetramethyl ether crystallises in well-formed, long needles, m. p. 232—234°, mixed m. p. with the isomeride 205—211°.

The compound,  $C_{11}H_3O_3(OMe)_3$ , formed on heating *isogalloflavin trimethyl ether*, separates from alcohol in colourless crystals, m. p. 130—134°.

The ether ester,  $C_{12}H_2O_3(OMe)_3$ , has m. p. 93—95°; the ether acid,  $C_{12}H_4O_3(OMe)_4$ , is colourless; it becomes coloured at 205°, m. p.

214—215° (decomp.). Heated at 210—220°, carbon dioxide is eliminated, and the compound,  $C_{11}H_8O_4(OMe)_4$ , m. p. 132—134°, is obtained.

Acetylpuropurogallin forms colourless plates, m. p. 181—183°. Tetramethylpuropurogallin is colourless, m. p. 91—92° (compare Perkin, Proc., 1905, 21, 211). E. F. A.

**Condensation Products of Gallic Acid Di- and Tri-methyl Ether. VII. Lactone Dyes.** JOSEF HERZIG and F. SCHMIDINGER (*Monatsh.*, 1910, 31, 819—826).—By the condensation of either gallic acid 3:4-dimethyl ether or gallic acid trimethyl ether by means of potassium persulphate, flavellagic acid tetramethyl ether (annexed formula), a yellow dye, is obtained.

When purified through the acetyl derivative, m. p. 237—238°, it crystallises in minute, sulphur-yellow needles, m. p. 270—271°.

By the action of potassium hydroxide and methyl sulphate, the lactone ring is opened, and flavellagic acid methyl ether ester (the completely methylated product), m. p. 81°, is obtained (compare Herzig and Tschernse, Abstr., 1908, i, 547). Diazomethane is entirely without action on the condensation product, although this readily converts flavellagic acid into the pentamethyl derivative. Apparently the resistant hydroxyl is rendered so by the presence of the methoxyl groups, and the same group is methylated at an early stage in the case of flavellagic acid itself. E. F. A.

**Synthesis of Glucosyringic Acid.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1910, [ii], 82, 271—274).—Methyl tetra-acetylglucosyringate,  $C_{24}H_{30}O_{14}$ , m. p. 106—107°, obtained by shaking a solution of methyl syringate in aqueous sodium hydroxide with ethereal  $\beta$ -acetobromoglucose for twenty-four hours, is hydrolysed by 6% barium hydroxide, whereby is obtained glucosyringic acid identical with that produced by the oxidation of syringin. C. S.

**Degradation of cycloGallipharic Acid by Oxidising Agents.** HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Arch. Pharm.*, 1910, 248, 398—420).—When cyclogallipharic acid, hydrolysed by sodium hydroxide, is heated for twelve hours on the water-bath with the gradual addition of 3.5% hydrogen peroxide, carbon dioxide and acetaldehyde are evolved, and, after acidification, a colourless, crystalline monobasic acid,  $C_{13}H_{12}O_8$ , m. p. 76°, is obtained, which develops a bluish-violet coloration with alcoholic ferric chloride. This reaction suggests that the acid is still a cyclic compound containing hydroxyl and carboxyl groups in the ortho-position; the acid is an oxidation product intermediate between cyclogallipharic acid and gallipharic acid, and consequently is called cyclomesogallipharic acid. When cyclogallipharic acid and an excess of sodium hydroxide on the water-bath are treated with 3.5% hydrogen peroxide until the bluish-violet coloration is no longer produced with ferric chloride, the products of

oxidation are found to be acetaldehyde, butyric acid, and gallipharic acid, m. p. 57.5° (not 54°).

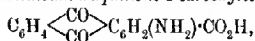
The oxidation of *cyclogallipharic acid* by sodium carbonate and 3% potassium permanganate has been shown to produce butyric and oxalic acids, glycerol, and gallipharic acid, m. p. 54° (Kunz-Krause and Schelle, Abstr., 1904, i, 587). The gallipharic acid is now shown, by analyses of the acid and of the sodium and silver salts, to be a mixture of about 75% gallipharic acid, m. p. 57.5°, and 25% of *gallipinic acid*,  $C_{14}H_{25}O_2$ , m. p. 49°, which is separable by dilute alcohol. In addition to these two, a small quantity of a third acid, *polycyclopharic acid*,  $C_{20}H_{30}O_3$ , m. p. 35°, has been isolated, which gives a Bordeaux-red coloration with ferric chloride, and develops in the liquid state an olive-green fluorescence and a pronounced odour of oranges. The greater part of these acids is absorbed by the hydrated manganese dioxide produced during the oxidation, and is extracted therefrom, after drying, by alcohol. The residue is freed from manganese dioxide by hot concentrated oxalic acid, and the residual yellow mass is purified by repeated solution in acetone and evaporation of the solvent, whereby a reddish-brown resin, *resocyclopharol*,  $C_{15}H_{24}O_3$ , m. p. 93°, is obtained, which has a pleasant odour of oranges, and in solution an acid reaction and olive-green fluorescence.

The oxidation of *cyclogallipharic acid* by alkaline potassium permanganate yields 28.16% of gallipinic and gallipharic acids, 44.96% of *resocyclopharol*, 16.20% of oxalic acid, 1.64% of butyric acid, and 2.20% of glycerol. C. S.

**Anthraquinone-2:3-dicarboxylic Anhydride.** CONRAD WILLGERODT and FRANCESCO MAFFEZZOLI (*J. pr. Chem.*, 1910, [ii], 82, 205—231).—The following results are the outcome of an unsuccessful attempt to obtain an anthraquinone-indigotin from anthraquinone-2:3-dicarboxylic anhydride by a method analogous to Heumann's synthesis.

Anthraquinone-2:3-dicarboxylic anhydride, which is precipitated almost quantitatively when the acid is boiled with acetic anhydride for fifteen minutes, is best converted into the imide by heating its intimate mixture with ammonium thiocyanate at 160—170° for five minutes, or with carbamide at 175—180° for one hour. *Anthraquinone-3-carbon-*

*amide-2-carboxylic acid*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2(CO \cdot NH_2) \cdot CO_2H$ , m. p. above 340°, prepared by dissolving the imide in dilute alkali at 40—50°, is converted into 3-aminoanthraquinone-2-carboxylic acid,

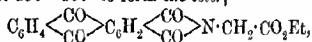


by oxidising its alkaline solution with freshly prepared sodium hypobromite, or, better, with 5.4% sodium hypochlorite, at 80—85°, or, quantitatively, with iodosobenzene; in all three cases a blood-red, crystalline alkali salt is precipitated, from which the amino-acid is liberated by hydrochloric acid and recrystallised from nitrobenzene; it then separates in orange-yellow needles. The amino-acid, the ammonium, sodium, silver, and barium salts of which are described, does not yield salts with acids, forms a yellow acetyl

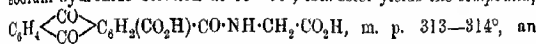
derivative, m. p. 248°, yields 2-aminoanthraquinone by the heating of its silver salt, and is converted into anthraquinone-2-carboxylic acid when the amino-group is replaced by hydrogen in the usual way. When heated with chloroacetic acid for half an hour, it yields, not the desired glycine derivative, but 3-chloroacetylaminanthraquinone-

2-carboxylic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$ , m. p. 350°,

which forms microscopic, orange crystals. When a pyridine solution of the imide mentioned above is diluted with an equal volume of alcohol and treated with alcoholic potassium hydroxide, the potassium derivative,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{NK}$ , is obtained as a brownish-grey powder, which is converted by water at 40–50° into potassium anthraquinone-3-carbonamide-2-carboxylate, and reacts with ethyl chloroacetate at 150–160° to form the ester,

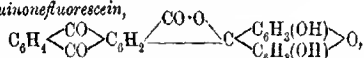


m. p. 241–242°. When treated with the calculated quantity of sodium hydroxide solution at 40–50°, this ester yields the compound,



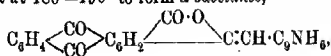
an alkaline solution of which is converted by sodium hypochlorite into anthraquinone-2-carboxylic acid, anthraquinone-2 : 3-dicarboxylic acid, and 3-a'-ipsoanthraquinone-2-carboxylic acid.

*Anthraquinonefluorescein*,



which is obtained by adding zinc chloride to an intimate mixture of resorcinol and anthraquinone-2 : 3-dicarboxylic anhydride at 150° and heating the mass at 180–190° for five to six hours (the purification of the product is troublesome), crystallises in yellow needles, m. p. above 380°. It forms in concentrated alkali a dark cherry-red, non-fluorescent solution, which becomes reddish-yellow by dilution and then exhibits a very feeble red fluorescence. The ammonium, silver, barium, calcium, magnesium, and lead salts of the fluorescein, which possesses feeble acid properties, are described. The diacetyl derivative, m. p. 259–260°, is hydrolysed by boiling alcoholic alkalis or by cold concentrated sulphuric acid, but not by boiling concentrated hydrochloric acid. When the powdered fluorescein is exposed in a desiccator to bromine vapour for three to four hours, it is converted into a red dibromoanthraquinonefluorescein,  $\text{C}_{23}\text{H}_{13}\text{O}_7\text{Br}_2$ , m. p. 313° (decomp.), which is soluble in alkalis and forms highly coloured salts. Tetrabromoanthraquinonefluorescein,  $\text{C}_{23}\text{H}_9\text{O}_7\text{Br}_4$ , m. p. 367° (decomp.), is obtained by adding the calculated amount of bromine to a cold alcoholic solution of anthraquinonefluorescein and precipitating the substance by water. The alkali salts of this and of the dibromo-derivative are dyes which have a great affinity for animal fibres.

Anthraquinone-2 : 3-dicarboxylic anhydride, quinaldine, and zinc chloride react at 180–190° to form a substance,



which crystallises in microscopic, yellow needles, does not melt below  $380^{\circ}$ , and dissolves unchanged in concentrated sulphuric acid.

C. S.

**Piperonylidene Diacetate.** JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 713—715).—Acetic anhydride in the presence of a drop of sulphuric acid converted piperonal into *piperonylidene diacetate*, which separated from alcohol in colourless, transparent crystals, m. p.  $51^{\circ}$ . After a time these crystals became opaque, their m. p. having changed to  $80^{\circ}$ . Various attempts to obtain again the modification with m. p.  $51^{\circ}$  were made, but proved unsuccessful.

A. J. W.

**Synthesis of a New Gallacetophenone Trimethyl Ether.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1910, [ii], 275—280).—3:4:5-Tri-methoxyphenyl methyl ketone,  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_3$ , m. p.  $73^{\circ}$ , is obtained by the action for fourteen days of ethereal diazomethane on a benzene solution of gallaldehyde trimethyl ether. A more convenient process starts from ethyl 3:4:5-trimethoxybenzoylacetate (best prepared by the condensation of ethyl acetate and methyl gallate trimethyl ether under the influence of sodium), which is converted into the ketone by heating for nine hours with 25% sulphuric acid. The *p*-nitrophenylhydrazone, m. p.  $195$ — $196^{\circ}$ , separates from hot alcohol in reddish-brown needles; the *semicarbazone* has m. p.  $178$ — $179^{\circ}$ .

C. S.

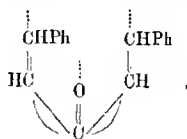
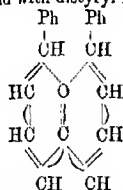
**Distribution of Affinity in Unsaturated Organic Compounds.** WALTHER BORSCHKE (*Annalen*, 1910, 375, 145—180).—In a conjugated system of two unsaturated groups, the residual affinities of the inner pair of unsaturated atoms neutralise each other, leaving free residual affinity only at the two external unsaturated atoms, where addition takes place. Thiele's conception, thus stated, is incorrect, for the inner pair of atoms still retain the power of increasing the mobility of univalent atoms attached to them through the intermediary of saturated multivalent atoms, and therefore still retain residual affinity. (According to Thiele, the increased mobility of a univalent atom, exhibited when the atom is attached to an unsaturated group through the intermediary of a saturated multivalent atom, as, for example,  $\cdots\text{C}:\text{O}\cdots$

$\text{OH}$ , is caused by the influence of the residual affinity of the unsaturated carbon atom on the hydroxylic oxygen atom, whereby the hold of the latter on the hydrogen is weakened.) The affinity (strictly speaking, that portion of the affinity which denotes the unsaturation) of an unsaturated atom in a conjugated system, therefore, is divided into three parts; for example, in the system,  $\text{C}:\text{C}:\text{C}:\text{C}$ , the affinity of

$\text{C}_\beta$  is divided into (i) the portion denoted in the double linking, (ii) the portion which is neutralised by the corresponding portion of the affinity of  $\text{C}_\gamma$ , (iii) the portion which persists as free residual affinity. At present little can be stated with regard to the quantitative proportions of these three parts; most probably they are different in each individual case. The distribution of the affinity in a conjugated system of

two unsaturated groups is such that there is a tendency for the neutralisation of the residual affinities of the inner pair of unsaturated atoms, and for the accumulation of residual affinity at the outer pair.

The distribution of the affinity in a conjugated system of three unsaturated groups forming a straight chain is very similar to the preceding, but the accumulation of residual affinity at the outer unsaturated atoms does not necessarily indicate great additive capacity, because in a chain of six atoms the last is near enough to the first for their residual affinities to more or less neutralise one another; for example, under suitable conditions, ethyl acetoacetate forms an additive compound with distyryl ketone, but not with dicinnamylideneacetone:



In conjugated systems containing "crossed" doubling linkings,  $\text{C}=\text{C}=\text{C}=\text{C}$ , there are three outer atoms at which the residual affinity can collect, and therefore the distribution of the affinity is more complicated. In the simple system  $\text{C}=\text{C}=\text{C}$ , the

affinity of the carbonyl carbon atom neutralises more or less that of the adjacent carbon atom; in the "crossed" system the central carbon atom, in order to neutralise the affinities of each of the adjacent carbon atoms, utilises more of its affinity; consequently, the oxygen atom has a greater amount of free residual affinity. There is more residual affinity at the three outer unsaturated atoms in a conjugated system of crossed double linkings than at the ends of a chain of three unsaturated groups forming a conjugated system; in the former system the neutralisation of the affinities of the three inner unsaturated atoms is less complete, the state of equilibrium first attained is more labile, and the system is more prone to enter into reaction. Such reactions will occur preferentially at the oxygen atom (or other multi-valent atom attached to the central carbon atom), the more so as the unsaturated atoms at the other two ends of the crossed system are so situated as to neutralise each other's residual affinity more or less completely.

The views developed above have been tested by experiments on the addition of ethyl acetoacetate and other compounds containing activated methylene groups to  $\alpha\beta$ -unsaturated ketones of the type of distyryl ketone, therefore, to substances containing the conjugated system of crossed double linkings,  $\text{C}=\text{C}=\text{C}=\text{C}$ .



According to the old view, a carbonyl group increases the additive power of a contiguous ethylenic linking without itself playing an active part in the addition. Consequently, there should be less tendency for the addition of a molecule, XY, to substances containing such a system than to substances containing the group  $\begin{array}{c} \text{C}:\text{C}:\text{C} \\ | \\ \text{O} \end{array}$ , because in the former case the activating influence of

the carbonyl group is diffused over two ethylenic linkings. When, however, one molecule of XY has been attached, the resulting system, CX·CY·CO·C:C, will have a greater additive power than the original system; consequently, the final product should be CX·CY·CO·CY·CX. According to the author's views, the system C:C·CO·C:C has a greater additive power than C:C·CO·C, and the final product will be CX·CY·CO·C:C. Now Knoevenagel and Speyer (Abstr., 1902, i, 226) have shown that equal molecular quantities of distyryl ketone and ethyl acetoacetate yield a substance, C<sub>28</sub>H<sub>24</sub>O<sub>4</sub>, which they formulate as CHPh·CH·CO·CH<sub>2</sub>·CHPh·CH(CO<sub>2</sub>Et)·COMe. Rabe and Elze (Abstr., 1902, i, 709) have shown that the substance has the constitution CHPh·CH·C(OH) $\begin{array}{c} \text{CH}_2\cdot\text{CHPh} \\ | \quad \diagup \\ \text{CH}_2\text{---CO} \end{array}$ CH·CO<sub>2</sub>Et.

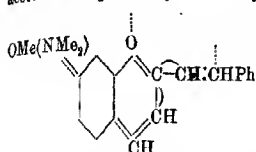
This constitution, which is confirmed by the author, is not a proof of the author's views, because even by the older theory the substance should be incapable of adding on a second molecule of ethyl acetoacetate, since it does not contain a carbonyl group in the immediate neighbourhood of the ethylenic linking. Similar cyclic β-ketone alcohols have been obtained from distyryl ketone and acetylacetone or benzoylacetone (the three β-ketone alcohols very easily lose a molecule of water, probably because the residual affinity of the nearer carbon atom in the ethylenic group renders the hydroxyl group more mobile by neutralising some of the affinity of the carbon atom to which it is attached). The author's view, however, is fully supported by the behaviour of ethyl benzoylacetate or ethyl malonate, which, even in excess, reacts with distyryl ketone to form the compounds



and CHPh·CH·CO·CH<sub>2</sub>·CHPh·CH(CO<sub>2</sub>Et)<sub>2</sub>. Dianisylideneacetone, tetramethyl *pp'*-diaminodibenzylideneacetone, and dicinnamylideneacetone do not react with ethyl acetoacetate under the conditions in which distyryl ketone reacts so easily; benzylideneanisylideneacetone-*p*-dimethylaminodistyryl ketone, and benzylideneacinnamylideneacetone do combine with 1 mol. of ethyl acetoacetate, but less readily than distyryl ketone. It follows from these six examples that the groups OMe·C<sub>6</sub>H<sub>4</sub>·, NMe<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·, and CHPh·CH· must in some way diminish the residual affinity, not only of the two external unsaturated carbon

atoms,  $\begin{array}{c} \text{C}:\text{C}:\text{C}:\text{C} \\ | \quad | \\ \text{---O---} \end{array}$ , but also of the carbonyl oxygen atom, the residual affinity of which influences the additive power of the two ethylenic linkings. The explanation in the case of dicinnamylideneacetone has been given above; in the cases of benzylideneanisylidene-

acetone and *p*-dimethylaminodistyryl ketone, the author suggests a



distribution of the affinity represented in the annexed formula.

The following compounds are described: Ethyl 3-phenyl-5-styrylcyclohexan-5-ol-1-one-2-carboxylate, prepared by Knoevenagel and Speyer (*loc. cit.*), is also obtained quantitatively when a mixture of

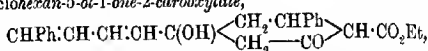
distyryl ketone, ethyl acetoacetate, and a little piperidine is heated on the water-bath for a few hours and is then kept at the ordinary temperature. It is best converted into ethyl 3-phenyl-5-styryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate by heating its alcoholic solution with sodium ethoxide or piperidine. The cyclohexene derivative yields a benzyl derivative, m. p. 128–129°, is converted by boiling glacial acetic and 20% sulphuric acids into 3-phenyl-5-styryl- $\Delta^5$ -cyclohexenone, m. p. 110–111°, and by prolonged treatment with alcoholic sodium ethoxide is changed into an isomeride, m. p. 159°, of unknown constitution. Ethyl  $\alpha$ -benzoyl- $\gamma$ -cinnamoyl- $\beta$ -phenylbutyrate,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}\text{CO}_2\text{Et}$ , m. p. 134°, obtained quantitatively by keeping a mixture of distyryl ketone, ethyl benzoylacetate, and a little piperidine in ether for many days; forms a dibromide, m. p. 180°, and is decomposed into its generators by heating with 10% sodium hydroxide. Distyryl ketone, acetylacetone, and a little piperidine yield 2-acetyl-3-phenyl-5-styrylcyclohexan-5-ol-1-one,  $\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{OH})\left\langle\begin{array}{l} \text{CH}_2\cdot\text{CHPh} \\ \text{CH}_2\text{—CO} \end{array}\right\rangle\text{CHAc}$ , m. p. 134–135°; a by-

product of the reaction is 2-acetyl-3-phenyl-5-styryl- $\Delta^5$ -cyclohexenone, m. p. 157–158°, which becomes the main product when the mixture is heated with alcohol for two to three days. 2-Benzoyl-3-phenyl-5-styrylcyclohexan-5-ol-1-one, m. p. 130°, and 2-benzoyl-3-phenyl-5-styryl- $\Delta^5$ -cyclohexenone, m. p. 171°, are obtained when a mixture of distyryl ketone, benzoylacetone, and a little piperidine in alcohol is heated for two hours and for one day respectively. Ethyl  $\gamma$ -cinnamoyl- $\beta$ -phenylpropane- $\alpha\alpha$ -dicarboxylate,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , m. p. 75°, obtained by heating a mixture of distyryl ketone, ethyl malonate, alcohol, and a little piperidine for two days on the water-bath, forms a phenylcarbamic acid hydrazone, m. p. 171°, and in alcoholic solution is hydrolysed by 25% sodium hydroxide at the ordinary temperature, yielding ultimately the free acid, m. p. 147–148° (decomp.), which is converted by heating into  $\gamma$ -cinnamoyl- $\beta$ -phenylpropionic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 153–159°.

Benzylideneanisylenacetone, ethyl acetoacetate, and a little piperidine yield ethyl 3-phenyl-5-*p*-methoxystyrylcyclohexan-5-ol-1-one-2-carboxylate, m. p. 142°, which loses  $\text{H}_2\text{O}$  when heated with 10% sodium hydroxide, ethyl 3-phenyl-5-*p*-methoxystyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p. 135°, being formed. *p*-Dimethylaminodistyryl ketone, m. p. 158°, which is best prepared by keeping a mixture of styryl methyl ketone, *p*-dimethylaminobenzaldehyde, and 10% sodium hydro-



oxide in 50% alcohol for a few weeks, reacts extremely slowly with ethyl acetoacetate in the presence of a little piperidine, yielding after seven days' heating a small quantity of a yellow, crystalline substance, m. p. 148°, which is presumably ethyl 3-phenyl-5-*p*-dimethylamino-styrylcyclohexan-1-one-2-carboxylate; when heated for two hours with alcoholic sodium ethoxide, however, the two substances react to form ethyl 3-phenyl-5-*p*-dimethylaminostyryl-Δ<sup>5</sup>-cyclohexen-1-one-2-carboxylate, which can only be isolated as the benzoyl derivative, m. p. 170—171°. A mixture of benzylidenecinnamylideneacetone, ethyl acetoacetate, and a little piperidine yields ethyl 3-phenyl-5-β-styryl-vinylcyclohexan-5-ol-1-one-2-carboxylate,



m. p. 144—145°, or ethyl 3-phenyl-5-β-styrylvinyl-Δ<sup>5</sup>-cyclohexen-1-one-2-carboxylate, m. p. 145°, accordingly as it is heated on the water-bath for a day and kept for several days or is heated with alcohol for the same time.

C. S.

**Action of Hydroxylamine on Ketones of the Type** CHR:CH:CH:CH:CO. ROBERTO CIUSA and A. BERNARDI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 58—62. Compare Abstr.; 1907, i, 62).—Styryl methyl ketone yields the oxime of m. p. 117° already known; phenyl styryl ketone, two isomeric hydroxylamineoximes, which are also known. Benzylidenecinnamylideneacetone gives a *hydroxylamineoxime*, m. p. 165°. Benzylidenepyrvic acid yields an *oxime*, m. p. 168°. When the sodium salt of cinnamylidenepyrvic acid is acted on by hydroxylamine in the absence of sodium acetate, it yields the sodium salt of an *oxime*, CHPh:CH:CH:CH:O(NH):CO<sub>2</sub>Na, from which, by loss of carbon dioxide, cinnamylidenecetonitrile is formed. In the presence of sodium acetate, however, an *oxime*, C<sub>23</sub>H<sub>29</sub>O<sub>2</sub>N<sub>2</sub>, m. p. 216—218°, is produced, probably by the union of two molecules of the esterified acid with two molecules of hydroxylamine. Ethyl cinnamylidenepyrvate gives an *hydroxylamineoxime*, C<sub>26</sub>H<sub>31</sub>O<sub>2</sub>N<sub>2</sub>, m. p. 213°, formed from 2 mols. of ester and 4 mols. of hydroxylamine.

The formation of oximes in some cases, and of hydroxylamineoximes in others is due to the different velocities with which the addition of hydroxylamine proceeds at the carbonyl group and at the system of double linkings. If the former is the greater, an oxime is formed, which although unsaturated does not react with hydroxylamine. The velocity of oxime formation is diminished when a methyl group of the ketone is replaced by a phenyl group (Petrenko-Kritschenko, Abstr., 1906, ii, 341), and this explains the formation of oximes from styryl methyl ketone and cinnamylideneacetone (Abstr., 1907, i, 62), whilst phenyl styryl ketone and cinnamylidenacetophenone yield hydroxylamineoximes.

R. V. S.

**Displacement of Alkyl Groups under the Influence of Aluminium Chloride. Acetyldiphenylmethanes and their Derivatives. Constitution of Some Derivatives of Diphenylmethane.** HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 789—796, 796—800).—Most of the data published in these two papers have been

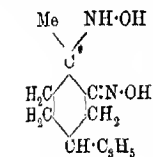
given already (Abstr., 1908, i, 277, 657). By the action of acetyl chloride on diphenylmethane in presence of aluminium chloride there is formed, in addition to 4-acetyl and 4:4'-diacetyl derivatives of the hydrocarbon, some acetophenone and a substance, m. p. 125°, which forms colourless crystals and appears to be a 4:4'-diacetylbenzyl-diphenylmethane,  $\text{CH}_2\text{Ph}\cdot\text{C}_6\text{H}_4\text{Ac}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Ac}$ . Details of the method of carrying out the operation and of separating and purifying the products are given.

4-Acetyldiphenylmethane, b. p. 209—210°/15 mm., forms colourless crystals from alcohol.

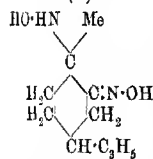
4:4'-Diacetyldiphenylmethane, b. p. 270—271°/15 mm., forms colourless crystals from warm alcohol. Its constitution is established by the observation that on oxidation with sodium hypobromite it yields benzophenone-4:4'-dicarboxylic acid, identified by means of its methyl ester, m. p. 231° (compare Limpricht, Abstr., 1900, i, 598).

T. A. H.

**Action of Hydroxylamine on Nitroschlorides and Nitrosates. I. *d*-Limonene-*o*-hydroxylamineoxime.** GUIDO CUSMANO (*Gazzetta*, 1910, 40, i, 602—613. Compare this vol., i, 182).—By the action of hydroxylamine on both  $\alpha$ - and  $\beta$ -*d*-limonene bisnitroschlorides, the same two *cis-trans*-isomeric hydroxylamineoximes (I. and II.) are obtained, and in addition a monoacidic base,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}_3$ . Which-



(I.)



(II.)

ever nitroschloride is employed, one of the isomerides appears in excess of the other; it has a positive optical rotation, and is therefore called the  $\alpha$ -form. Like the isomeride hydroxylaminocarboxime (compare Harries and Mayrhofer, Abstr., 1899, i, 624), the two substances are soluble in acids and in alkalis, and reduces Fehling's solution in the cold, but they are stable towards nitrous acid, do not give oxidation products, and do not condense with aldehydes. In alkaline solution they are converted rapidly into a salt (decomposed by carbon dioxide) of an isomeric yellow compound, which is soluble in acids, but does not reduce Fehling's solution, and, moreover, gives a blue coloration with diphenylamine and a violet coloration with phenol. By the action of acids the compound is converted into the original hydroxylamineoxime.

$\alpha$ -Limonenehydroxylamineoxime hydrochloride,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}_3\cdot\text{HCl}\cdot\text{H}_2\text{O}$ , forms large, prismatic crystals, m. p. 142°,  $[\alpha]_D^{25} - 35\cdot30^\circ$ . When kept in a vacuum desiccator it loses a molecule of water, and then has m. p. 153° (decomp.). The free  $\alpha$ -hydroxylamineoxime,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}_3$ , forms large, colourless, prismatic crystals, which soften towards 145° and decompose at 150°; it has  $[\alpha]_D^{25} + 17\cdot73^\circ$ . The  $\beta$ -hydroxylamineoxime is obtained in very small quantity along with the  $\alpha$ -form. It has m. p. 173° (decomp.), and gives a hydrochloride, m. p. 152°. In the above preparation the hydrochloride of a base,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{N}_3\cdot\text{HCl}$ , is also formed in small quantity. It crystallises in needles or flat prisms,

m. p. about  $212^{\circ}$  (decomp.);  $[\alpha]_D^{25} -57.88^{\circ}$ . The base,  $C_{10}H_{18}O_2N_2$ , has m. p. towards  $210^{\circ}$  (decomp.), and scarcely reduces Fehling's solution in the warm. All the above compounds are similarly obtained from  $\beta$ -d-limonene bisnitrosochloride. The yellow isomeride of the  $\alpha$ -hydroxylamineoxime is readily formed from the latter substance, especially if impure or in solution. It is prepared by precipitating alkaline solutions of the substance with carbon dioxide. It has m. p.  $167.5^{\circ}$  (decomp.), and the molecular weight required by the formula  $C_{10}H_{18}O_2N_2$ . Treatment with acids converts it into the  $\alpha$ -hydroxylamineoxime. When this change is effected with ethereal hydrogen chloride, a substance,  $C_{10}H_{20}O_2N_2Cl_2$ , is also obtained in yellow prisms, m. p.  $130^{\circ}$  (decomp. explosively). It is unstable, gives an intense blue diphenylamine reaction, does not dissolve in cold alkalis, and does not yield the hydroxylamineoxime when treated with hydrogen chloride in ether.

R. V. S.

**Mechanism of the Opening of the cyclobutane Ring in Derivatives of Pinene.** GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1910, [v], 10, ii, 63—68. Compare this vol., i, 574, and preceding abstract).— $\alpha$ -Pinenehydroxylamineoxime yields, with alkalis, nitrosopinene, with acids, hydroxydihydrocarvone. According to Wallach's theory of the mechanism of the opening of the cyclobutane ring in pinene and in sabinene derivatives (Abstr., 1908, i, 429), the formation of nitrosopinene as an intermediate product would be expected in the latter case, but the author shows that nitrosopinene does not yield hydroxydihydrocarvone when acted on by acids. Similarly, the salts of pineneisnitroamineoxime yield, when treated with alkalis, both nitrosopinene and hydroxypinocampnoneoxime. Neither of these compounds can be converted into the other under the conditions of the experiment, but dilute acids transform hydroxypinocampnoneoxime into the isomeric hydroxydihydrocarvone. It appears, therefore, that Wallach's theory is untenable in this case, for which the author provides the explanation that the loss of the elements of water so disturbs the molecule as to cause rupture of the bridge at the same time, whilst the displacement of hyponitrous acid does not.

R. V. S.

**Constitution of Fenchone. IV.** LOUIE BOUYEAULT and F. LEVALLOIS (*Bull. Soc. chim.*, 1910, [iv], 7, 807—810).—In previous papers (this vol., i, 572, 573, 627) the steps in the gradual degradation of fenchone to apofenchone have been detailed, and in this communication an account is given of the oxidation of this hydrocarbon, on which a preliminary paper has been already published (Abstr., 1908, i, 193).

The products of the oxidation of apofenchone by alkaline permanganate are (1) a neutral substance, probably a glycol; (2) a small quantity of a mixture of fatty acids, and acids possessing a pyruvic odour; (3) a mixture of acids (b. p.  $70-160^{\circ}/10$  mm.) containing 90% of isopropylsuccinic acid, and (4) a mixture of acids (b. p.  $160-165^{\circ}/10$  mm.). The fourth fraction contains three acids: (1) a hydroxy-acid, yielding on oxidation by lead peroxide and sulphuric acid a ketonic substance of the type  $R \cdot COMe$ ; (2) a ketonic acid, furnishing a semi-

carbazone, m. p.  $140^{\circ}$ , and (3) a ketonic acid, yielding a semicarbazone  $C_{10}H_{19}O_2N_3$ , and which on oxidation with sodium hypobromite gives  $\beta$ -isopropylglutaric acid. As already indicated (*loc. cit.*), these results support Semmler's formula for fenchone.

T. A. H.

**Causes of Geraniol Odours.** GÉZA AUSTERWEIL and G. COCHIN (*Compt. rend.*, 1910, 151, 440—441. Compare this vol., i, 572).—The group  $CH \cdot CRR' \cdot OH$  appears to be necessary for the presence of a geraniol odour. 1-Methylgeraniol, b. p.  $105-106^{\circ}/18$  mm., prepared by the application of Grignard's reaction to citral, has a pronounced odour of polargonium leaves; this is scarcely modified by the introduction of a second methyl group. 1:1-Dimethylgeraniol, h. p.  $104^{\circ}/16$  mm., was obtained by oxidising the foregoing compound and submitting the ketone to Grignard's reaction. The odour of 1-ethylgeraniol and 1:1-dimethylgeraniol, h. p.  $123-125^{\circ}/20$  mm., resembles that of the primary alcohol. 1-isoButylgeraniol, h. p.  $115^{\circ}/26$  mm., and 1-phenylgeraniol, b. p.  $135-138^{\circ}/22$  mm., have a less intense odour, that of the latter being somewhat rose-like. Methylcyclogeraniol, h. p.  $98^{\circ}/20$  mm., has scarcely any geraniol odour.

W. O. W.

**Oil of Copaiba.** ERNST DEUSSEN and ALFRED HAHN (*Chem. Zeit.*, 1910, 34, 873).—The caryophyllene from oil of copaiba is not a definite product, but yields on distillation several fractions with an increasing rotatory power, thus distinguishing it from the caryophyllene obtained from oil of cloves, the higher fractions of which show a decreasing rotatory power. No permanent blue coloration is obtained by acting on the caryophyllene from copaiba with nitrosyl chloride, whereas that from cloves yields a blue nitrosite.

Both oils, however, contain sesquiterpenes of a preponderating bicyclic nature.

L. DE K.

**Gurjun Oil (So-called East Indian Copaiba Oil).** ERNST DEUSSEN and HANS PHILLIPP (*Chem. Zeit.*, 1910, 34, 921—923).—An investigation as to the nature of gurjun oil, which seems to belong to the series of sesquiterpenes.

Utz's statement that gurjun oil has a much higher boiling point than oil of copaiba is not quite correct, and this fact should be taken into consideration when testing copaiba balsam for gurjun balsam and operating, according to Utz, on the distillate. The colour reaction (whether working on the balsam itself or on the volatile oil therefrom) due to Turner and approved of by Utz, and again strongly recommended by the authors, is as follows: 3 to 4 drops of the sample of copaiba balsam are dissolved in 3 c.c. of glacial acetic acid, 1 drop of a 10% solution of sodium nitrite is added, and the mixture is carefully poured on to 2 c.c. of sulphuric acid. In presence of gurjun balsam a dark violet colour will be noticed in the acetic acid layer.

L. DE K.

**New Components of Oil of Jasmine Flower.** F. ELZE (*Chem. Zeit.*, 1910, 34, 912).—In addition to the substances found in oil of jasmine flower by Hesse (Aber., 1899, i, 377, 441; 1900, i, 48, 454;

1901, i, 220, 732), the author finds that it contains *p*-cresol and geraniol. L. DE K.

[Essential] Oil of *Robinia Pseudocacia*. F. ELZE (*Chem. Zeit.*, 1910, 34, 814).—The author prepared a specimen of the oil by extracting the blossoms of the plant with very volatile solvents; the crude oil was then purified by treatment with alcohol. The oil had  $D_{20}^{25}$  1.05, and the ester content calculated as methyl anthranilate amounted to 9%. The alcoholic solution had a distinct bluish fluorescence, and contained much indole. Under 5 mm. pressure, the oil passed over between 60° and 150°.

When submitted to the usual tests for essential oils, it was found to contain benzyl alcohol,  $\alpha$ -terpineol, heliotropine, methyl anthranilate, linalool, indole, and ketone or aldehyde substances having the odour of peaches. The presence of nerol is also probable, and pyridine bases could be isolated. L. DE K.

Nerol and Farnesol in Java Canang Oil. F. ELZE (*Chem. Zeit.*, 1910, 34, 851).—The oil contains about 0.2% of nerol and about 0.3% of farnesol. L. DE K.

Honduras Balsam. ALEXANDER TSCHIRCH and J. O. WERDMÜLLER (*Arch. Pharm.*, 1910, 248, 420—430).—A pale Honduras balsam, represented by three samples having  $D$  1.0886, 1.0905, and 1.0884 respectively, and a pronounced odour of storax, has mean acid number 32.67 and saponification number 173.2. The balsam is dissolved in ether and shaken with 1% sodium carbonate, whereby cinnamic acid is extracted together with an ester which yields cinnamic acid and honduroresinol by hydrolysis. The ethereal solution is next treated with 1% potassium hydroxide, whereby a further quantity of honduroresinyl cinnamate is obtained, and also a substance,  $(C_{32}H_{58}O_4)_x$ , which melts above 300°, does not respond to the phytosterol reactions, and shows the properties of a resin; it is called  $\beta$ -honduroresin. The ethereal solution is finally evaporated, leaving a yellow oil (so-called "cinnamëin") representing more than half the weight of the balsam. A portion of the oil yields by distillation cinnamic acid and an oil from which a small quantity of a hydrocarbon, honduran,  $C_{18}H_{30}$ , b. p. 154—155°, can be isolated. Another portion of the "cinnamëin" is hydrolysed by 1% potassium hydroxide, whereby cinnamyl alcohol, cinnamic acid, honduran, a hydrocarbon,  $(C_8H_{14})_x$ , b. p. 140—155°, and distyrene are produced.

A dark Honduras balsam, represented by two samples,  $D$  1.0897 and 1.0915, has acid number 29.9 and saponification number 153.9. It has been examined in the preceding way. The sodium carbonate extract contains cinnamic acid and the cinnamate of a honduroresinol,  $(C_{16}H_{26}O_2)_x$ , m. p. 141°. The potassium hydroxide extract contains cinnamic acid, honduroresinyl cinnamate, and a resin, m. p. 169—172°, which is not identical with  $\beta$ -honduroresin. The "cinnamëin" is hydrolysed by aqueous potassium hydroxide, and then distilled with steam. The non-volatile oil is dissolved in alcohol and cooled by solid carbon dioxide, whereby crystals are obtained, which are collected,

wasbed with alcohol, and treated with warm petroleum. The portion insoluble in the petroleum is a resin, m. p.  $163^{\circ}$ . When cooled in carbon dioxide, the petroleum solution deposits crystals of an unsaturated dihydric alcohol, *handurool*,  $C_{17}H_{16}O_2$ , m. p.  $42.5^{\circ}$ , which forms a *dibenzooate*, m. p.  $38^{\circ}$ . The alcoholic mother liquor contains phenylpropyl alcohol and distyrene. C. S.

**Cabureiba Balsam.** ALEXANDER TSCHIRCH and J. O. WERDMÜLLE (Arch. Pharm., 1910, 248, 431—432).—Schaer has recently described a rare balsam obtained from Brazil, and probably identical with *Piso's* cabureiba balsam (Guibourt's haume de Pérou brun or rouge en coques). Its ethereal solution yields to 1% sodium carbonate, benzoic (but not cinnamic) acid and a resinous substance, from which, after hydrolysis by 1% potassium hydroxide, benzoic acid, vanillin, and a *cabureibaresinolannol*,  $C_{14}H_{18}O_4$ , have been isolated. The balsam does not contain a "cinnamöin." C. S.

**Benin Copal.** M. KAHAN (Arch. Pharm., 1910, 248, 433—442).—Benin copal is completely soluble in a mixture of ether and alcohol; alcohol alone dissolves about 60%, and ether 45.5%. The dried substance sinters at  $120^{\circ}$ , and forms a clear, transparent mass at  $166^{\circ}$ . It has acid number 101.15 (direct) and 118.75 (indirect), saponification number 134.4 (cold, after twenty-four hours), 143.5 (cold, after forty-eight hours), 149.8 (hot, after one hour), 146.3 (hot, after two hours), and iodine number 61.02. It does not yield succinic acid by dry distillation. An ethereal extract of Benin copal is shaken successively with 1, 2, and 5% ammonium carbonate, sodium carbonate, and potassium hydroxide; the residual solution, after removal of the ether, is distilled with steam, whereby an ethereal oil, b. p.  $180-256^{\circ}$ , and a yellow resin,  *$\alpha$ -benincopaloresin*, m. p.  $164-166^{\circ}$ , are obtained. The ammonium carbonate extract contains *benincopallic acid*,  $C_{17}H_{32}O_4$ , m. p.  $137^{\circ}$ , acid number 183.4 (direct) and 180.6 (indirect), saponification number 194.6 (cold, after twenty-four hours), 196.0 (cold, after forty-eight hours), 196.7 (hot, after one hour), 200.2 (hot, after two hours), iodine number 83.43, which forms a lead salt insoluble in alcohol. The sodium carbonate extract contains  *$\alpha$ -benincopallic acid*,  $C_{13}H_{22}O_6$ , m. p.  $81^{\circ}$ , acid number 191.8 (direct) and 188.9 (indirect), saponification number 198.3 (cold) and 197.4 (hot), iodine number 87.24, and  *$\beta$ -benincopallic acid*,  $C_{20}H_{30}O_2$ , m. p.  $119^{\circ}$ , acid number 185.2 (direct) and 184.1 (indirect), saponification number 193.3 (cold) and 194.6 (hot), iodine number 84.84; the lead salts of the two acids are insoluble in alcohol, but the former acid dissolves in glacial acetic acid. The potassium hydroxide extract contains *benincopalenic acid*,  $C_{27}H_{48}O_2$ , m. p.  $101^{\circ}$ , acid number 147.0 (direct) and 145.6 (indirect), iodine number 63.88.

The residue of Benin copal insoluble in ether is dissolved almost completely by a mixture of ether and alcohol. The solution, after being shaken with 1% potassium hydroxide, contains  *$\beta$ -benincopaloresin*,  $C_{12}H_{20}O_{10}$ , a white, amorphous substance. The potassium hydroxide extract contains  *$\alpha$ -benincopallic acid*,  $C_{21}H_{30}O_3$ , m. p.  $187^{\circ}$ , acid number 172.2 (direct) and 170.8 (indirect), saponification number 180.6 (cold) and 177.8 (hot), iodine number 76.51;  *$\beta$ -benincopallic*

acid,  $C_{15}H_{28}O_3$ , m. p. 193—197°, acid number 216.3 (direct) and 216.3 (indirect), iodine number 97.73, and  $\gamma$ -benincopaloresin,  $C_{18}H_{30}O_4$ , m. p. 192—195°; the last is insoluble in alcohol, whilst of the two acids the former yields a lead salt which is insoluble in alcohol.

C. S.

**Accra Copal.** M. KAHAN (*Arch. Pharm.*, 1910, 248, 443—450).—Accra copal is completely soluble in a mixture of ether and alcohol; alcohol alone dissolves about 54% and ether 50%. The substance has m. p. 106—156°, acid number 121.8 (direct) and 126.4 (indirect), saponification number 133.4 (cold) and 140.0 (hot), and iodine number 58.54.

An ethereal extract of Accra copal is shaken successively with ammonium carbonate, sodium carbonate, and potassium hydroxide; the residual solution contains  $\alpha$ -accracopaloresin,  $C_{15}H_{26}O_3$ , m. p. 178—180°, and an ethereal oil, b. p. 164—266°. The ammonium carbonate extract contains accracopallic acid,  $C_{21}H_{34}O_8$ , m. p. 104—106°, acid number 177.5 (direct) and 175.0 (indirect), saponification number 180.7 (cold) and 180.6 (hot), iodine number 75.31. The sodium carbonate extract contains  $\alpha$ -accracopallic acid,  $C_{18}H_{26}O_6$ , m. p. 152—155°, acid number 194.6 (direct) and 192.5 (indirect), saponification number 195.3 (cold) and 196.4 (hot), iodine number 85.49, and  $\beta$ -accracopallic acid,  $C_{16}H_{22}O_6$ , m. p. 144—148°, acid number 189.0 (direct) and 186.9 (indirect), saponification number 194.6 (cold) and 195.3 (hot), iodine number 86.86. The potassium hydroxide extract contains  $\alpha$ -accracopalenic acid,  $C_{16}H_{20}O_6$ , m. p. 142—146°, and  $\beta$ -accracopalenic acid,  $C_{12}H_{20}O_3$ , m. p. 150—152°, acid number 246.4, which are separated by lead acetate.

The residue of the Accra copal insoluble in ether is dissolved in a mixture of ether and alcohol, and the solution is shaken with 1% potassium hydroxide; the ethereal alcoholic solution retains  $\beta$ -accracopaloresin,  $C_{18}H_{26}O_3$ , m. p. 197—199°, whilst the alkaline extract contains accracopallic acid,  $C_{14}H_{20}O_3$ , m. p. 122—124°, acid number 214.9 (direct) and 214.2 (indirect), saponification number 226.8 (cold) and 228.2 (hot), iodine number 98.29, and  $\gamma$ -accracopaloresin,  $C_{16}H_{20}O_3$ , m. p. 184—186°, which is insoluble in alcohol.

C. S.

**Manila Copal.** GEORGE F. RICHMOND (*Philippine J. Sci.*, 1910, [A], 5, 177—201).—It is shown that the Manila copal produced in the Philippines is of two kinds, "recent" and semifossil, and is derived from a single species, *Agathis alba* (*Dammara orientalis*). The constants of the two kinds of resin are quite similar, and they both consist of a mixture of resin acids with a lactone (?), neutral saponifiable resin, and more or less volatile oil. The only well-defined solid product obtained from the resin is a crystalline acid of the formula  $C_{10}H_{16}O_2$ . On distillation in steam the resin yields volatile oil in quantity, which depends partly on the age of the resin and partly on its physical condition. The volatile oil,  $D_4^{20}$  0.865,  $n_D^{20}$  1.4648,  $[\alpha]_D^{20}$  -26.55°, contains pinene. The resin dissolves completely in alcohol, and addition of potassium hydroxide to such a preparation yields (A) a solution containing volatile oil and soluble

potassium resinsates, and (B) a precipitate containing insoluble potassium resinsates and some neutral resin.

From A the following substances were obtained: (1) a lemon-yellow, volatile oil possessing a terpene-like odour; (2) an acid,  $C_{10}H_{15}O_2$ , m. p. 185–187°, which is dextrorotatory and crystallises from dilute alcohol in colourless needles, and (3) an amorphous acid,  $C_{22}H_{34}O_4$ , which can be distilled almost unchanged at a pressure of 3–5 mm., yielding a clear, amber-coloured product.

From B there were isolated (1) an amorphous acid,  $C_{22}H_{34}O_4$ , m. p. above 220°; (2) a lactonic substance, which on digestion with hot aqueous solutions of potassium hydroxide furnishes the potassium salt of a resin acid similar to that yielding the insoluble resinate referred to above, and (3) neutral unsaponifiable resin. These results, especially as regards the properties of the acids, are not in accordance with those recorded by Tschirch and Koch for Manila copal derived from *Dammara orientalis* (Abstr., 1902, i, 478).

On dry distillation the copal yielded about 70% of greenish-yellow oil, b. p. 140–350°, and left a pitch-like residue (compare succeeding abstract). On “melting” various samples of the resin at temperatures ranging from 250–325°, the loss varied from 13.3 to 17.4%. The “melted” resin was similar in composition to the raw material, but contained less neutral resin, so that the latter only appears to undergo change in the ordinary process of making copal varnish. The remainder of the paper deals with copal varnish manufacture.

T. A. H.

**Destructive Distillation of Manila Copal.** BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, [A], 5, 203–217. Compare preceding and succeeding abstracts).—On heating, Manila copal froths until the temperature reaches 330°, when the resin melts and quiet ebullition sets in. Up to 330° the products evolved include resin oil, pinene,  $\beta$ -pinene, limonene, dipentene, camphene, water, formic and acetic acids, methyl alcohol, acetone, formaldehyde, pyruvaldehyde, furfuraldehyde, carbon dioxide, acetaldehyde (?), and saturated and unsaturated hydrocarbons. Above 330°, considerable quantities of carbon monoxide and some ethylene and propylene are formed, but the other products of this further stage in destructive distillation were not studied. The remainder of the paper deals with (1) the effect of heat in rendering Manila copal soluble and suitable for varnish manufacture, and (2) its behaviour with various solvents.

T. A. H.

**Oxidation of Manila Copal by the Air.** BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, [A], 5, 219–227. Compare two preceding abstracts).—The well-known fact that the older copal resins (“fossil” copals) are better suited for varnish manufacture than the “recent” kinds has led the author to investigate the changes which take place when Manila copal is exposed to air and light. The results show that the resin absorbs oxygen somewhat rapidly, forming organic peroxides (compare Fahrion, Abstr., 1902, i, 165; 1904, i, 332; 1907, i, 329), and evolves carbon dioxide, formaldehyde, formic acid, and hydrogen



peroxide. The evolution of carbon dioxide is probably due to the formation and subsequent decomposition of peroxides, both in the cases of Manila copal and colophony. These changes are accompanied by an increase in the Koettstorfer number of the resin. The change in the Koettstorfer number, which accompanies prolonged maceration of many resins in potassium hydroxide in alcohol, is, however, not due to oxidation effects during the experiment, but probably to the gradual saponification of lactones and the breaking down of organic peroxides. The oxidation of Manila copal is accelerated by sunlight. Under certain conditions the resin gives off vapours which affect a photographic plate. The mixed resin acids of Manila copal show similar changes on exposure to air, but more slowly.

T. A. H.

**Oleo-Resin of *Pinus insularis*.** BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, [4], 5, 229—231).—The turpentine oil distilled from this oleo-resin had  $D_{20}^{20}$  0.8593,  $n_D^{20}$  1.4656,  $[\alpha]_D^{20}$  +26.5 at 30°, distilled to the extent of 96% between 154° and 165.5°, and consisted mainly of pinene.

The colophony left on distillation of the oleo-resin consisted almost entirely of abietic acid, m. p. 154—156°, had Koettstorfer number 170.2, and gave the Liebermann-Storch reaction.

T. A. H.

**Preparation of True Arbutin.** HENRI HÉRISSEY (*Compt. rend.*, 1910, 151, 444—447; *J. Pharm. Chim.*, 1910, [vii], 2, 248—253).—

Fifteen grams of commercial arbutin (containing methylarbutin) are dissolved in 95% alcohol (500 c.c.) and treated with 10 grams of potassium hydroxide in 125 c.c. of alcohol. When clear, the supernatant liquid is removed, and the crystalline precipitate washed with alcohol (20 c.c.), dissolved in 75 c.c. of boiling alcohol and acetic acid (7 c.c.), and treated with calcium carbonate (5 grams). After removing the alcohol, the residue is lixiviated with water (100, 50, and 50 c.c.). The filtrate is treated with calcium carbonate (2 grams), evaporated to dryness, and the product crystallised from ethyl acetate. Pure arbutin crystallises with  $1H_2O$ , and is identical with the glucoside obtained from the pear tree by Bourquelot (this vol., ii, 742). The anhydrous substance has  $[\alpha]_D^{20}$  -63.45°.

W. O. W.

**A New Glucoside Hydrolysed by Emulsin in *Menyanthes trifoliata*.** MARC BRIDEL (*J. Pharm. Chim.*, 1910, [vii], 2, 165—167).

—The glucoside, which it is proposed to call *meliatin*, m. p. 222° (corr.),  $[\alpha]_D^{20}$  -81.94° in alcohol, is crystalline. Its solutions are hydrolysed by emulsin, becoming bluish-green and dextrorotatory, and producing a reducing sugar. It is not identical with Kromayer's *menyanthin* (*Arch. Pharm.*, 1865, 174, 35, and Lendrich, *Abstr.*, 1892, 1262).

T. A. H.

**The Chlorophyll Group. VII. Chlorophyllan, *allo*Chlorophyllan, and Chlorophyllpyrrole.** HENRYK MALARSKI and LEON MARCZLEWSKI (*Biochem. Zeitsch.*, 1910, 27, 246—260. Compare this vol., ii, 362).—It is claimed that the substances described under the name of chlorophyllan, phyllogen, and phaeophytin are identical.

They were prepared by the methods described by Schunk and Marchlewski and Willstätter, and the various preparations yielded the same amount of phytol on hydrolysis, and yielded chlorophyllanic acids similar to the phytochlorins of Willstätter. A preparation was also obtained which did not agree in properties with Willstätter's phytochlorin-*d*. Chlorophyllan also contains in small quantities (especially that derived from maple leaves) another product, *allo-chlorophyllan*, of which the authors give some spectrum absorption measurements. They have also succeeded in preparing from chlorophyllpyrrole, azo-colouring matters with benzenediazonium chloride identical with those obtained from hæmopyrrole.

S. B. S.

**Benzoylloxanthone.** ERNST ZERNER (*Monatsh.*, 1910, 31, 797-798).—Graebe and Ehrhard (*Abstr.*, 1882, 1301) describe dibenzoylloxanthone as yellow or brown, m. p. 214°. On benzoylating oxanthone with benzoyl chloride and potassium hydroxide, the dibenzoyl derivative is obtained colourless, m. p. 221-222° (corr.), together with about 10% of yellow *monobenzoylloxanthone*, m. p. 156-159° (corr.), in which the benzoyl group occupies position 7. On benzoylating in acid solution, only dibenzoylloxanthone results.

E. F. A.

[Preparation of Halogen Derivatives of 6-Amino-3-keto-(1)-thionaphthen and Nitroisatins.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 221529 and 221530).—When the products obtained by condensing 6-amino-3-keto (1)-thionaphthen in acetic acid solution with nitroisatins or amino-oxindoles are treated with halogens either with or without previous reduction, brownish-yellow dyes are obtained.

6-Amino-3-keto-(1)-thionaphthen, m. p. 165°, is a brownish-grey powder, soluble in hot water.

The nitration of isatin with fuming nitric acid (D 1.5) yields a *nitroisatin*, which crystallises from acetic acid in yellow needles, m. p. 253-255°; potassium nitrate with concentrated sulphuric acid may also be employed, but under these conditions the product has m. p. 248-250°.

The second patent deals with the products obtained when the 6-amino-3-keto-(1)-thionaphthen in the foregoing condensation is replaced by *m*-acetylaminophenylthioglycol-*o*-carboxylic acid, the components being heated together during three hours in the presence of acetic anhydride; the *product* is a brown powder, which becomes yellow on treatment with sodium hyposulphite, and on halogenation yields vat dyes. The reduction of these compounds previous to halogenation is also described in the patents.

F. M. G. M.

**Ergoxanthin.** WILLIAM T. WENZEL (*Amer. J. Pharm.*, 1910, 82, 410-416).—The author does not consider that the preparation of the alkaloids of ergot in a purer form justifies the supersession of the names *ecboline* and *ergotine* originally applied by him to these alkaloids (*Amer. J. Pharm.*, 1864, 36, 193; compare Kobert, *Abstr.*, 1885, 821; Barger, *Trans.*, 1907, 91, 337, and Barger and Dale, *Abstr.*, 1907, i, 79).

**Ergoxanthein** was prepared from Squibb's fluid extract of ergot by shaking this with ether after preliminary purification with alcohol and chloroform. It is an orange-yellow, amorphous substance, giving blood-red solutions with alkalis, developing a deep orange colour with nitric acid and a blood-red coloration with sulphuric acid. It gives an orange-yellow precipitate with lead acetate and a yellow precipitate with phosphotungstic acid. The absorption spectra of solutions of ergoxanthein are recorded which may be of value for the estimation and toxicological detection of ergot. The substance is physiologically active, and causes a rise in blood pressure.

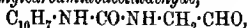
T. A. H.

**Hydroxylupanine.** A. BECKEL (*Arch. Pharm.*, 1910, 248, 451—457).—The properties and behaviour of natural hydroxylupanine, already recorded by Bergh (*Arch. Pharm.*, 1904, 242, 416) are confirmed, and the formation of *d*-lupanine by reduction is proved conclusively by an examination of the aurichloride, platinichloride, and thiocyanate.

C. S.

**Compounds of  $\alpha$ -Naphthylcarbamide with some Physiologically Important Substances.** CARL NEUBERG and ELSE HIRSCHBERG (*Biochem. Zeitsch.*, 1910, 27, 339—347).—This reagent gives sparingly soluble  $\alpha$ -naphthylhydantoic acids with amino-acids, and  $\alpha$ -naphthylurethanes with alcohols and phenols. The former can be prepared by shaking aqueous solutions of the reacting substance together in the presence of alkalis; the latter must be prepared in absence of water, and are obtained by heating the reacting substances together. The following substances were obtained: *glyceryl tri- $\alpha$ -naphthylcarbamate*,

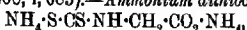
$\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ ,  
n. p. 279—280°; the *di- $\alpha$ -naphthylurethane* of glyceric acid,  
 $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CO}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ ,  
n. p. 289—290°; *phenyl  $\alpha$ -naphthylcarbamate*, m. p. 136—137°; *o-tolyl  $\alpha$ -naphthylcarbamate*, m. p. 145°; *m-tolyl  $\alpha$ -naphthylcarbamate*, m. p. 135—136°; *p-tolyl  $\alpha$ -naphthylcarbamate*, m. p. 150—151°; *carvacryl  $\alpha$ -naphthylcarbamate*, m. p. 287—288°; *saligenyl  $\alpha$ -naphthylcarbamate*, n. p. 283°; *cinnamyl  $\alpha$ -naphthylcarbamate*, m. p. 119—120°; *menthyl  $\alpha$ -naphthylcarbamate*, m. p. 128°; *l-bornyl  $\alpha$ -naphthylcarbamate*, m. p. 132°; *isobornyl  $\alpha$ -naphthylcarbamate*, m. p. 129°;  *$\alpha$ -terpinyl  $\alpha$ -naphthylcarbamate*, m. p. 151—152°; *cyclohexyl  $\alpha$ -naphthylcarbamate*, m. p. 139—140°; *furfuryl  $\alpha$ -naphthylcarbamate*, m. p. 133°; *cholesteryl  $\alpha$ -naphthylcarbamate*, m. p. 175—176°;  *$\alpha$ -naphthylcarbamido-*D*-glucosamine*,  $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}(\text{CHO})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ , m. p. 134—236°;  *$\alpha$ -naphthylcarbamidoacetaldehyde*,



amorphous.

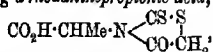
S. B. S.

**Substituted Rodanic Acids and their Aldehyde Condensation Products.** X. RUDOLF ANDREASCH (*Monatsh.*, 1910, 31, 785—795. Compare Abstr., 1908, i, 683).—*Ammonium diethiocarbaminacetate*,



prepared by the interaction of glycine, carbon disulphide, and alcoholic ammonia, forms colourless needles, m. p. 110° (decomp.).

*Ammonium- $\alpha$ -dithiocarbaminopropionate*, prepared in a similar manner from alanine, has m. p. 128—129° (decomp.). It reacts with ethyl chloroacetate, forming  *$\alpha$ -rhodaninepropionic acid*,



separating in granular crystals, m. p. 147°. Condensation products with aldehydes are formed on heating the components in acetic acid.

*$\beta$ -Benzylidene- $\alpha$ -rhodaninepropionic acid* forms bright yellow granules or needles, m. p. 191°.  *$\beta$ -Dimethylaminobenzylidene- $\alpha$ -rhodaninepropionic acid* forms a crust of dark reddish-brown crystals, m. p. 210—220°; it dyes the skin, wool, and silk orange-red, but the colour is not fast.  *$\beta$ -p-Hydroxybenzylidene- $\alpha$ -rhodaninepropionic acid* forms a crust of light chrome-yellow needles, which sinter at 190°, m. p. 205—210°, forming a red sublimate.

*$\beta$ -Methylenedioxybenzylidene- $\alpha$ -rhodaninepropionic acid*, prepared by condensation with piperonal, forms orange-yellow granules or a yellow, crystalline powder, m. p. 197—199°.

*Rhodanineglycylglycine*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N} < \begin{matrix} \text{CS}\cdot\text{S} \\ \text{CO}\cdot\text{CH}_2 \end{matrix}$ , is prepared by the interaction of glycylglycine, ammonia, and carbon disulphide, the corresponding *dithiocarbamate* being first formed and immediately condensing with ethyl chloroacetate. A honey-yellow syrup was obtained, which condensed with benzaldehyde to *benzylidene-rhodanineglycylglycine*. It crystallises in greenish-yellow plates or needles, m. p. 190° (sinters at 180°).

In the case of asparagine, aspartic and glutamic acids, and leucine, both the rhodanines and their aldehyde condensation products could only be obtained as syrups. E. F. A.

**Formation of Imino-ethers by Direct Alkylation of Acid Amides with Methyl Sulphate.** MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 37—45).—Imino-ethers may be obtained directly from the free acid amides by alkylation with methyl sulphate at temperatures below 100°, showing that the amide itself may react in the iminohydrin form, just as does its silver salt. Both aliphatic and aromatic acid amides, as well as the thio-acid amides, react in this way, giving rise to the methyl hydrogen sulphates of the imino-ethers. These compounds generally separate as an oil, which may afterwards crystallise, when the amide is heated in a reflux apparatus with methyl sulphate. In some cases the imino-ether was set free by treatment with sodium carbonate solution, extracted with ethyl ether, and the hydrochloride or other salts prepared.

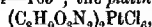
*Thiobenziminomethyl ether methyl hydrogen sulphate*,  $\text{C}_6\text{H}_5\text{NS}\cdot\text{HSO}_4\text{Me}$ , and *thio-p-toluiminomethyl ether methyl hydrogen sulphate*,  $\text{C}_6\text{H}_4\text{NS}\cdot\text{HSO}_4\text{Me}$ ,

were prepared from thiobenzamido and thio-p-toluamide respectively; they form long, colourless prisms. The free ethers separated as an oil on the addition of sodium carbonate solution, but could not be isolated, as they decompose into methyl mercaptan and cyaphenine or cyatoline.

*Benziminomethyl ether methyl hydrogen sulphate* was obtained from

benzamide as a deliquescent substance; it could not be purified from the admixed benzamide. The hydrochloride (Abstr., 1895, i, 522) and also the *platinichloride*,  $(C_6H_5ON)_2PtCl_6$ , were prepared.

*o*-Nitrobenziminomethyl ether,  $C_8H_9O_3N_2$ , was obtained from *o*-nitrobenzamide in colourless crystals, m. p.  $87^\circ$ . The *hydrochloride* forms slender needles, m. p.  $164-165^\circ$ ; the *platinichloride*,



m. p.  $162^\circ$ , was also prepared. The hydrochloride was transformed into *o*-nitrobenzamidina, which is a yellow liquid of alkaline reactions; its *platinichloride*,  $(C_7H_8O_2N_3)_2PtCl_6$ , was analysed.

*Benzenphenyliminomethyl ether*,  $C_9H_9ON$ , was obtained from acetanilide as a colourless, viscid oil. The *hydrochloride* is decomposed by water; the *platinichloride*,  $(C_9H_9ON)_2PtCl_6$ , was analysed.

Formamide gave rise to hygroscopic, scaly crystals of *formiminomethyl ether methyl hydrogen sulphate*, from which formiminomethyl ether was liberated by alkali. *Acetiminomethyl ether* is an oil, b. p.  $63-65^\circ$ . Qualitative proof of the formation of *propioiminomethyl ether* from propionamide was obtained.

T. S. P.

**Methylpyridonium Picrate.** G. TOTANI and Z. HOSHIAI (*Zeitsch. physiol. Chem.*, 1910, 68, 85. Compare Abstr., 1909, ii, 327).—*Methylpyridonium picrate*,  $C_5H_5NMe \cdot O \cdot C_6H_2(NO_2)_3$ , crystallises from water in slender, yellow needles, m. p.  $212^\circ$ . Its solubility in 100 parts of solvent at the ordinary temperature is: water 1.092, alcohol 0.358, ether 0.017.

J. J. S.

[Preparation of Dinitronaphthylpyridinium Derivatives.] FARBENFABRIKEN VORM. FREIDR. BATER & Co. (D.R.P. 222130. Compare Zincke, Abstr., 1904, i, 448).—The interaction of secondary dihydroindoles with cyanopyridinium or dinitrophenylpyridinium salts, whereby red to violet basic dyes are obtained, has previously been recorded. When the halogen-free product, red needles, m. p.  $214^\circ$ , prepared by the action of pyridine (2 mols.) on 1-chloro-2:4-dinitronaphthalene (1 mol.) in aqueous alcoholic solution, is treated with  $\alpha$ -methyl-dihydroindole in glacial acetic acid, and hydrochloric acid dropped in, a mixture of 2:4-dinitro- $\alpha$ -naphthylamine and a dye is obtained; these are separated by extracting the latter with boiling water, and subsequently precipitating with salt; it forms a brownish-red powder.

F. M. G. M.

**Racemic Liquid Compounds.** ALBERT LADENBURG (*Compt. rend.*, 1910, 151, 283-284).—Four crystallisations of the *d*-camphor sulphate of *r*-pipecoline suffice to obtain the *L* base in a state of purity. The author shows that the freezing-point curve for mixtures of *d*- and *L*-pipecoline agrees with the existence of a racemic liquid form of this substance.

W. O. W.

[Preparation of Anthraquinoneacridones.] FRITZ ULLMANN (D.R.P. 221853).—When the anilinoanthraquinonecarboxylic acids of general formula  $CO_2H \cdot C_6H_4 \cdot NHR$  (where R = anthraquinone or a substituted anthraquinone residue) are treated with reagents, such as

phosphorus pentachloride and aluminium trichloride, they are converted into anthraquinoneacridones.

*Anthraquinoneacridone* is prepared by treating  $\alpha$ -anilinoanthraquinonecarboxylic acid (obtained from  $\alpha$ -nitro- or  $\alpha$ -chloro-anthraquinone and anthranilic acid) with phosphorus pentachloride in benzene solution, and heating the red *acid chloride* thus obtained with aluminium trichloride; it crystallises from aniline in violet-red, glistening needles with a metallic lustre; its solution in concentrated sulphuric acid is red.

The *methylanthraquinoneacridone* prepared from the condensation product of anthranilic acid with 1-chloro-4-methylanthraquinone has similar properties.

The *product* obtained by treating  $\beta$ -anilinoanthraquinonecarboxylic acid (prepared from  $\beta$ -aminoanthraquinone and *o*-chlorobenzoic acid) with concentrated sulphuric acid is a very sparingly soluble, yellow powder, which dissolves in concentrated sulphuric acid with a brownish-yellow colour.

F. M. G. M.

**New Group of Substituted Dioxindoles.** MORITZ KOUN (Monatsh., 1910, 31, 747–751).—Isatin reacts with the Grignard reagent, only one of the carbonyl groups being affected, and on hydrolysis compounds of the type  $C_6H_3 \begin{smallmatrix} < CR(OH) \\ < NH \end{smallmatrix} > CO$  are obtained.

The *phenyl* derivative forms long, white, lustrous needles, m. p.  $213^\circ$ , to a yellowish-brown liquid.

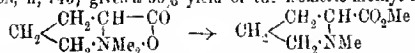
The *benzyl* derivative crystallises in colourless needles, m. p.  $171$ – $173^\circ$ .

The  *$\alpha$ -naphthyl* derivative becomes coloured above  $200^\circ$ , m. p.  $233^\circ$ .

The *p-bromophenyl* derivative separates in wool-like needles, m. p.  $193$ – $195^\circ$  (decomp.). All these substituted dioxindoles are stable in the atmosphere.

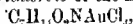
E. F. A.

**Conversion of Stachydrine into the Isomeric Methyl Hygrate.** GEORG TRIER (Zeitsch. physiol. Chem., 1910, 67, 324–331. Compare Willstätter, Abstr., 1902, i, 266; Willstätter and Kahn, *ibid.*, 1904, i, 235, 560).—When distilled under reduced pressure, stachydrine (this vol., ii, 743) gives a 66% yield of the isomeric methyl hygrate,



Other products are trimethylamine and a little hygric acid.

So far it has not been found possible to transform the methyl ester into stachydrine. The *aureichloride* of the methyl ester,



crystallises in rectangular plates, m. p.  $84$ – $86^\circ$ , and when boiled with excess of hydrochloric acid yields hygric acid aureichloride.

When the hydrochloride of the ethyl ester of stachydrine (containing also stachydrine hydrochloride) is distilled, the products are hygric acid, its methyl and ethyl esters, and their decomposition products.

Hygric acid is non-poisonous, whereas its methyl ester is a strong poison.

J. J. S.

### Dissociation Constant of Tropine and its Variation with Temperature. HARALD LUNDÉN (*J. Chim. Phys.*, 1910, 8, 331—336).

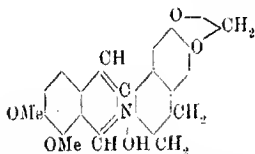
—The molecular conductivities of solutions of tropine hydrochloride at 10°, 25°, and 50° show that tropine is a fairly strong base, so that hydrolytic dissociation of the hydrochloride does not occur. The molecular conductivity of free tropine at infinite dilution is calculated to be 0.17 at 10°, 0.227 at 25°, 0.326 at 50°. The variation of conductivity of the hydrochloride with temperature is in agreement with Johnston's logarithmic theorem (*Abstr.*, 1909, ii, 854).

The dissociation constant of tropine calculated from measurements on the free base is  $1.87 \times 10^{-4}$  at 10°,  $2.74 \times 10^{-4}$  at 25°, and  $3.89 \times 10^{-4}$  at 50°. These figures are of an entirely different order from that obtained by Veley by the colorimetric method, namely,  $1.10^{-8}$  at 17° (*Trans.*, 1909, 96, 3). They are, however, of the same order as the dissociation of piperidine ( $1.6.10^{-8}$  at 25°) and coniine ( $1.3.10^{-8}$  at 25°), to which tropine is allied. The heat of dissociation of tropine calculated from the dissociation constant is negative, but appreciably greater than the negative heat of dissociation of piperidine.

The conductivity of mixtures of sodium hydroxide and tropine shows that tropine possesses no acidity, its constant of acidic dissociation being less than  $10^{-14}$ . R. J. C.

### Constitution and Derivatives of Berberine. FRANZ FALTIS (*Monatsh.*, 1910, 31, 557—581).

—When Freund and Beck's  $\alpha$ -phenyl-dihydroberberine (*Abstr.*, 1905, i, 151) is repeatedly oxidised with potassium permanganate at the ordinary temperature, appreciable amounts of 2-benzoyl-3:4-dimethoxybenzoic acid are formed. This reaction supports the formula (annexed formula) suggested several years ago (*Abstr.*, 1906, i, 979) and supported recently by Perkin (*Trans.*, 1910, 97, 321). If berberine had the constitution originally suggested by Perkin, the product of oxidation would be 2-benzoyl-5:6-dimethoxybenzoic acid.



2-Benzoyl-3:4-dimethoxybenzoic acid,  $C_{16}H_{12}Bz(OMe)_2 \cdot CO_2H$ , crystallises in colourless needles, m. p. 190—191°, and is not decomposed when heated with concentrated hydrochloric acid at 150°. Its constitution follows from the fact that, when fused for two minutes with potassium hydroxide, the products are benzoic and protocatechuic acids. Boiling hydriodic acid converts the benzoylated acid into a compound,  $C_{27}H_{20}O_8$ , m. p. 223—224°. This is probably an additive compound of the 3:4-dihydroxy-2-benzoylbenzoic acid with 2:3-dihydroxybenzophenone. An impure 4-hydroxy-2-benzoyl-3-methoxybenzoic acid,  $C_{15}H_{12}O_5$ , is formed when hydrogen chloride is led through a suspension of the dimethoxy-acid in boiling hydriodic acid for twenty-four hours.

Gadamer (*Abstr.*, 1902, i, 555; 1905, i, 369) states that the reaction between berberine and potassium hydroxide solution is analogous to that between benzaldehyde and alkali, and that the products are

dihydroberberine and oxyberberine. The author claims that the reaction is similar to that between quinoline methiodide and alkali (Döcker, Abstr., 1903, i, 516, 718), and that the products are oxyberberine and tetrahydroberberine. The reduction product differs from pure tetrahydroberberine (m. p. 167.5—168.5°) prepared from berberine by the action of zinc dust and glacial acetic acid; (a) its hydrochloride contains water of hydration, and (b) it is more readily transformed into berberine, for example, when its hydrochloride is heated at 100°.

The golden-yellow colour of Gadamer's oxyberberine is completely removed when the product is heated with zinc dust and glacial acetic acid. It is then obtained in glistening, colourless needles, m. p. 200—200.5°, with all its other properties intact. It would thus appear that only those berberine derivatives which contain a non-hydrogenated pyridine ring are coloured.

*Oxyberberine hydrochloride* and *hydrobromide* are readily obtained as lemon-yellow, amorphous precipitates when hydrogen chloride or bromide is passed into a chloroform solution of the base, but immediately yield colourless oxyberberine when treated with water. The hydrochloride,  $C_{20}H_{17}O_2N \cdot HCl$ , softens at 200°, and melts at about 240°. The *stannichloride*,  $C_{20}H_{17}O_2N \cdot HCl \cdot SnCl_4$ , forms a stable, yellow, amorphous precipitate.

*Methyluoroxyberberine*,  $C_{19}H_{15}O_2N$ , obtained by passing hydrogen chloride into a boiling glacial acetic acid solution of oxyberberine or by heating oxyberberine hydrobromide in boiling xylene, crystallises in glistening, silky needles, m. p. 248°. It does not yield salts, and gives an intense violet-blue coloration with 50% sulphuric acid and a drop of nitric acid.

A black powder is formed when oxyberberine is boiled for a long time with hydriodic or hydrobromic acid. Methyluoroxyberberine contains a hydroxy-group, and yields an *acetyl* derivative,  $C_{21}H_{17}O_3N$ , m. p. 242—244°.

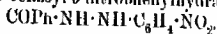
*Bromomethyluoroxyberberine*,  $C_{19}H_{14}O_2NBr$ , prepared by the action of bromine on a chloroform solution of methyluoroxyberberine, crystallises from hot xylene in slender needles, m. p. 239° (decomp.), and yields an *acetyl* derivative,  $C_{21}H_{16}O_3NBr$ , m. p. 225—227° (decomp.).

Bromine reacts with a chloroform solution of oxyberberine, yielding *bromo-oxyberberine tribromide*,  $C_{18}H_{13}O_3NBr(OMe)_2 \cdot HBr \cdot Br_3$ , as golden-yellow needles, m. p. 210° (decomp.).

The tribromide when boiled with xylene yields bromomethyluoroxyberberine, and when treated with water yields *bromo-oxyberberine*,  $C_{20}H_{16}O_3NBr$ , which crystallises from alcohol in large, colourless prisms, m. p. 184—185°.

J. J. S.

**Conversion of Hydrazidines into Hydrazines.** GIACOMO POZZIO (*Gazzetta*, 1910, 40, i, 433—435).—The hydrazidines previously described (this vol., i, 443) when heated for some hours with dilute acids (10%) evolve ammonia, and are converted into the corresponding acylarylhydrazines; thus *o*-aminobenzaldehyde-*o*-nitrophenylhydrazone (*loc. cit.*) yields benzoyl-*o*-nitrophenylhydrazine,

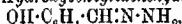




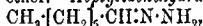
This reaction forms an argument for the formula  $\text{NH}_2\cdot\text{CR}\cdot\text{N}\cdot\text{NH}_2$  in preference to  $\text{NH}\cdot\text{CR}\cdot\text{NH}\cdot\text{NH}_2$  for the hydrazidides. R. V. S.

**Benzylidenehydrazines.** HARTWIG FRANZEN and TH. EICHLER (*J. pr. Chem.*, 1910, [ii], 82, 241—251).—At high temperatures or in boiling xylene, benzylidenehydrazines of the type  $\text{CHR}\cdot\text{N}\cdot\text{NH}_2$  react as such or decompose into aldehydes and hydrazine, the latter of which then attacks one or more of the other substances present; for example, benzylidenehydrazine and phthalimide at 130—140° or in boiling xylene yield benzaldazine and phthalhydrazide; benzylidenehydrazine and carbon disulphide form benzaldazine and hydrazine dithiocarbazinate, the latter being obtained by the action of hydrazine and carbon disulphide; benzylidenehydrazine and ethyl benzoate at 160—170° yield benzaldazine, benzhydrazide, and benzylidenebenzhydrazide; benzylidenehydrazine, benzoyl chloride, and pyridine in dry ether at 0° yield benzaldazine, benzylidenebenzhydrazide, and dibenzhydrazide.

The following benzylidenehydrazines are prepared by Curtius and Franzen's method of treating aldehydes with a boiling solution of hydrazine hydrate: *m*-Hydroxybenzylidenehydrazine,



m. p. 104.5° (picrate, m. p. 187°; phenylthiosemicarbazide, m. p. 194°), from *m*-hydroxybenzaldehyde, m. p. 205°; *p*-hydroxybenzylidenehydrazine, m. p. 139° (picrate, m. p. 222°; phenylthiosemicarbazide, m. p. 225°), from *p*-hydroxybenzaldehyde, m. p. 232°; *o*-aminobenzylidenehydrazine, m. p. 62° (dipicrate, m. p. 188°), from *o*-aminobenzaldehyde; *m*-methoxybenzylidenehydrazine, b. p. 174—175°/21 mm. (phenylthiosemicarbazide, m. p. 153°), from *m*-methoxybenzaldehyde; *p*-methoxy- and *p*-ethoxybenzaldehydes yield the corresponding benzylidenehydrazines, which, however, revert to the original benzaldehydes during the process of isolation by ether. Heptylidenehydrazine,



b. p. 164—165°/12 mm., was prepared from heptaldehyde and aqueous hydrazine hydrate.

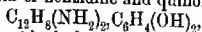
The water formed during the production of mixed aldehydes by the condensation of benzylidenehydrazines and aldehydes complicates the reaction by attacking the benzylidenehydrazine, whereby a second aldehyde is formed and hydrazine hydrate, which then reacts with the aldehyde to produce a third aldehyde. The authors prevent the by-reactions by using, instead of the aldehyde, its condensation product with aniline; thus, benzylidenehydrazine and ethereal *m*-nitrobenzylideneaniline yield *s*-*m*-nitrodibenzylidenehydrazine; *m*-hydroxybenzylideneaniline and ethereal benzylidenehydrazine yield *m*-hydroxydibenzylidenehydrazine, m. p. 162°; *p*-hydroxybenzylidenehydrazine and benzylideneaniline yield *p*-hydroxydibenzylidenehydrazine, m. p. 239—240°.

C. S.

**Additive Compounds of Aromatic Amines with Phenols.** JOSEF DÖLLINGER (*Monatsh.*, 1910, 31, 643—656. Compare Dyson, *Trans.*, 1883, 43, 466; Hebebrand, *Abstr.*, 1883, 61; Philip, *Trans.*, 1903, 83, 814; Philip and Smith, *ibid.*, 1905, 87, 1735; Kremann, *Abstr.*, 1906, ii, 266; Schreinmakers, *Abstr.*, 1899, ii, 739; 1900, ii,

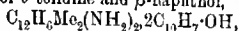
(135).—Additive compounds of quinol,  $\alpha$ - and  $\beta$ -naphthol with benzidine, *o*-tolidine, and *o*-dianisidine can be prepared by mixing together hot saturated aqueous solutions of the components. They are all practically insoluble in water, are resolved into their components when boiled with dilute acids or alkalis, and with the exception of the compound of *o*-tolidine and  $\alpha$ -naphthol, contain an equal number of hydroxyl and amino-groups. Most of the compounds give characteristic colorations with ferric chloride in aqueous solution.

The additive compound of benzidine and quinol,



is best prepared from cold alcoholic solutions, and forms colourless, glistening, rhombic plates, m. p.  $230^\circ$  (decomp.). The additive compound of benzidine and  $\beta$ -naphthol,  $\text{C}_{12}\text{H}_8(\text{NH}_2)_2 \cdot 2\text{C}_{10}\text{H}_7\text{OH}$ , forms colourless, iridescent plates, m. p.  $177^\circ$ .

The amount of quinol or  $\beta$ -naphthol in an aqueous solution can be determined by adding benzidine solution and weighing the product (97% of the theoretical). The additive compound of *o*-tolidine and quinol,  $\text{C}_{12}\text{H}_8\text{Me}_2(\text{NH}_2)_2 \cdot \text{C}_6\text{H}_4(\text{OH})_2$ , can be prepared from ethereal solutions, and forms microscopic needles with a red colour. It has m. p.  $158^\circ$  after sintering at  $140^\circ$ . The additive compound of *o*-tolidine and  $\alpha$ -naphthol,  $\text{C}_{12}\text{H}_8\text{Me}_2(\text{NH}_2)_2 \cdot \text{C}_{10}\text{H}_7\text{OH}$ , crystallises from dilute alcohol in reddish-coloured needles, m. p.  $90^\circ$ . The additive compound of *o*-tolidine and  $\beta$ -naphthol,



crystallises in glistening plates, m. p.  $96^\circ$ . The additive compound of dianisidine and quinol,  $\text{C}_{12}\text{H}_8(\text{OMe})_2(\text{NH}_2)_2 \cdot \text{C}_6\text{H}_4(\text{OH})_2$ , separates from a mixture of benzene and light petroleum as pale lilac-coloured crystals, m. p.  $157^\circ$  (decomp.). The additive compound of dianisidine and  $\beta$ -naphthol,  $\text{C}_{12}\text{H}_8(\text{OMe})_2(\text{NH}_2)_2 \cdot 2\text{C}_{10}\text{H}_7\text{OH}$ , crystallises in long, reddish-coloured needles, m. p.  $96^\circ$ . The additive compound of  $\alpha$ -naphthylamine and  $\alpha$ -naphthol,  $\text{C}_{10}\text{H}_7\text{NH}_2 \cdot \text{C}_{10}\text{H}_7\text{OH}$ , forms pale lilac-coloured needles, m. p.  $60^\circ$ , and is decomposed by boiling water. The additive compound of  $\alpha$ -naphthylamine and  $\beta$ -naphthol crystallises in glistening, rose-coloured prisms, m. p.  $73$ – $74^\circ$ . The additive compound of  $\beta$ -naphthylamine and  $\beta$ -naphthol forms colourless prisms, m. p.  $125$ – $126^\circ$ .

The following pairs of substances do not form sparingly soluble additive compounds:  $\beta$ -Naphthylamine and  $\alpha$ -naphthol,  $\alpha$ -naphthylamine and quinol, benzidine and catechol, benzidine and resorcinol.

Some of the compounds appear to be acidic, others basic, and still others amphoteric.

J. J. S.

**Preparation of Condensation Products in the Anthracene Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 222205).—The condensation of aminoanthraquinones with halogen ketones yielding products of the type  $\text{A}\cdot\text{NH}\cdot\text{R}\cdot\text{CO}\cdot\text{R}\cdot\text{NH}\cdot\text{A}$  has been previously described (this vol., i, 397); the reaction has now been extended to halogen diketones of the general type  $\text{H}\cdot\text{R}\cdot\text{CO}\cdot\text{CO}\cdot\text{R}\cdot\text{H}$  ( $\text{H}$ =halogen), which yield with aminoanthraquinones a new series of compounds of the general formula  $\text{A}\cdot\text{NH}\cdot\text{R}\cdot\text{CO}\cdot\text{CO}\cdot\text{R}\cdot\text{NH}\cdot\text{A}$  ( $\text{A}$ =anthraquinone residue).

4:4'-Dichlorobenzil (50 parts) is boiled with 1-aminoanthraquinone (100 parts) and sodium carbonate (20 parts) in nitrobenzene solution in the presence of cupric oxide until the reaction is complete, when, on cooling, the product separates in brown needles. The nitrobenzene can be replaced by other indifferent solvents, and the copper oxide by cuprous chloride.

F. M. G. M.

**Preparation of Condensation Products in the Anthracene Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 222206).—An extension of the type of condensation described in the previous patent; in the present case the general reaction is that by which one or more anthraquinone residues are connected through an imino-group with one or more phenanthraquinone radicles. Two mols. of a monohalogenated phenanthraquinone may condense with 2 mols. of a mono- or with 1 mol. of a di-aminoanthraquinone; similarly, one molecular proportion of a dihalogenated phenanthraquinone may combine with 3 mols. of a mono- or with 1 mol. of a di-aminoanthraquinone. These condensations take place in boiling nitrobenzene solution in the presence of copper oxide and sodium carbonate or acetate.

The product from monobromophenanthraquinone (3 parts) and 1-aminoanthraquinone (2.4 parts) is a violet-brown powder, insoluble in water, alkali, and dilute acids; it yields a violet-brown colour with concentrated sulphuric acid, and violet-brown with boric acid.

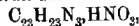
The products from monobromophenanthraquinone (4.8 parts) and 1:5-diaminoanthraquinone (2 parts), from dibromophenanthraquinone (5 parts) and 1-aminoanthraquinone (10 parts), and from dichlorophenanthraquinone (3 parts) and 1-aminoanthraquinone (3 parts) were also prepared.

The dibromophenanthraquinone was obtained by brominating phenanthraquinone in nitrobenzene solution at 100°, the product separating in crystalline form from the hot solution; it crystallises from acetic acid in long, glistening, golden needles, m. p. 388°.

Dichlorophenanthraquinone was analogously prepared in the presence of a halogen carrier; it crystallises from acetic acid in red needles, m. p. above 300°.

F. M. G. M.

**Tetramethylchrysaniine.** OTTO FISCHER and EDG. SCHMIDT (*J. pr. chem.*, 1910, [ii], 82, 288—291).—The by-product obtained when 2-aminotetramethyl-4':4''-diaminotriphenylmethane is oxidised by arsenic acid (Abstr., 1882, 833) is produced in larger quantity when a boiling solution of the leuco-base in xylene is treated with yellow mercuric oxide for twelve to fifteen hours. The suggestion that it is tetramethylchrysaniine, m. p. 229—230°, is proved to be correct. The *platinichloride* and *picrate* are described; the *nitrate*,

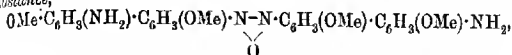


is readily soluble in water.

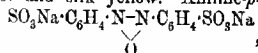
C. S.

**Preparation of Azoxy-compounds.** FRITZ REITZENSTEIN (*J. pr. Chem.*, 1910, [ii], 82, 232—270).—By the oxidation of certain aromatic mono- or di-amines by warm alkaline potassium ferricyanide, the author has obtained dyes which he regards as containing the azoxy-

group. The dyes are produced in satisfactory yield, are substantive in character, and generally can be diazotised and combined on the fibre. After the removal of the dye, chlorine is passed into the mother liquor, which can then be utilised again; thus dianisidine gives the substance,



a dark red powder, which dyes wool and silk yellow. Aniline-*p*-sulphonic acid yields the substance,



and 2:6-dibromoaniline-4-sulphonic acid a corresponding substance, which is brick-red and dyes wool a more intense yellow than the preceding substance. Similar azoxy-dyes are produced from benzidinesulphonedisulphonic acid, benzidinesulphonic acid, naphthidine, *oo'*-diaminodiphenic acid, *p*-phenylenediaminesulphonic acid, atoxyl (*p*-aminophenylarsinic acid), diaminostilbenedisulphonic acid, diaminotolan, and 4:4'-diaminodiphenylmethane.

C. S.

*endo*Bisazo-derivatives of Diphenylmethane. HENRI DUVAL (*Bull. Soc. chim.*, 1910, [iv], 7, 852-861. Compare this vol., i, 559, 588).—The general character of this investigation has been discussed already and most of the results recorded (Abstr., 1907, i, 663; 1908, i, 658, 706). The following new compounds are described: Bisazo-diphenylmethane-4:4'-dicarboxylic acid (*loc. cit.*) on reduction with zinc and hydrochloric acid furnishes *bishydrazodiphenylmethane-4:4'-dicarboxylic acid*, which is amorphous, but yields a *tetracetyl* derivative, crystallising in small, yellow needles.

T. A. H.

Hemielastin. ELKAN WECHSLER (*Zeitsch. physiol. Chem.*, 1910, 67, 486-488).—Hemielastin (Horbaczewski, Abstr., 1883, 927) when hydrolysed with sulphuric acid gave the following numbers: ammonia, 0.4; humin nitrogen I, 3.1; humin nitrogen II, 4.9; histidine, 1.0; arginine, 4.2; monoamino-acids, 71.1; lysine, 3.4% of the total nitrogen.

These correspond with arginine, 1.86; histidine, 0.53; lysine, 2.48, and ammonia, 0.05% of the original hemielastin.

J. J. S.

Guanylic Acid from the Pancreas. II. HERMANN STEUDEL and P. BAIGL (*Zeitsch. physiol. Chem.*, 1910, 68, 40-51. Compare Steudel, Abstr., 1908, i, 70).—Bang's  $\beta$ -guanylic acid is regarded as the acid potassium salt of guanylic acid. When repeatedly dissolved in water and precipitated, it becomes more soluble, owing to loss of potassium. The formula suggested is  $\text{C}_{10}\text{H}_{13}\text{O}_8\text{N}_5\text{PK}$ . A corresponding barium salt has been prepared. The amounts of guanine and pentose formed on hydrolysis agree with the amounts required for such a formula.

The pentose is shown to be arabinose.

Levene's guanosino could not be isolated (compare Abstr., 1909, i, 620).

J. J. S.

**Non-existence of Free or Combined Lecithins in the Yolk of Eggs.** N. ALBERTO BARRIERI (*Compt. rend.*, 1910, 151, 405-407. Compare Abstr., 1907, ii, 708).—From experiments on the yolks of 3000 eggs, the author has been unable to obtain any evidence for the existence of lecithins in this material. The fatty matters can be separated in a state of purity by the aid of neutral solvents. They contain nitrogenous substances, but these can be removed by simple dialysis, and chlorine was not detected amongst them. The fats yield on hydrolysis nothing but glycerol and fatty acids. The phosphorus, moreover, was entirely dialysable, and appears to be present chiefly in the form of phosphates.

The portion of the yolk soluble in ether, commonly described as consisting of lecithins, yielded only small quantities of a *platinichloride*, m. p. 215°, containing 4.43% of nitrogen. The same salt was obtained from those constituents of the yolk soluble in water and alcohol.

W. O. W.

**Iodoproteins.** CARL NEUBERG (*Biochem. Zeitsch.*, 1910, 27, 261-270).—The author gives an account of some attempts to prepare iodine-containing hydrolysis products from iodoproteins, using iodo-glucadin, a derivative of wheat proteins. The method attempted was to partly hydrolyse the iodoprotein with sulphuric acid at about 37°, and then to digest the hydrolysis mixture with pancreatin, and to separate the iodo-derivative by fractionating out on copper. He also gives an account of similar experiments carried out by L. Scott on iodo-spongin. He draws attention to an error in the estimation of iodine in organic compounds when nitrate is employed in the destruction of organic matter, and water vapour is then distilled through the iodine-containing mixture in the presence of ferric chloride into potassium iodide solution. If nitrate is employed, nitric oxide, free chlorine (from the aqua regia), etc., interfere with the reaction.

S. B. S.

**Gelatin and Tannin.** HANS TRUNKEL (*Biochem. Zeitsch.*, 1910, 23, 458-492).—Gelatin and tannin can be precipitated quantitatively from solution. The same quantity of lime (1 gram) requires more tannin for precipitation (0.7 gram) when fresh than when the solution has stood for twenty-four hours (0.4 gram). By warming the solution, however, the original proportions are re-attained. By this means a calcium tannate stable to water is obtained. If excess of tannin is employed, a precipitate is obtained from which tannin can be continually extracted by water. Neither the water-stable nor water-unstable precipitates can be separated into the components by alcohol, which extracts only 97% alcohol. From the gelatin residue only 6% of a gelatinising residue can be obtained. By treatment of both tannates with water or alcohol, a small amount of gallic acid is formed. The author shows that the quantitative relationships between the gelatin and tannin in the precipitates formed in various dilutions follow approximately the exponential adsorption equation, and he concludes that chemical processes play but a subordinate part in the reaction between the two substances.

S. B. S.

## General and Physical Chemistry.

The Refraction and Dispersion of Argon and Redeterminations of the Dispersion of Helium, Neon, Krypton, and Xenon. CLIVE CUTHBERTSON and MAUD CUTHBERTSON (*Proc. Roy. Soc.*, 1910, A, 84, 13—15. Compare Abstr., 1909, ii, 105).—The mean of seven experiments gave 1.00028230 for the refractive index of argon for the wave-length 5461. The dispersion observed between the wave-lengths 6438.5 and 4799.9 (7 lines) agreed with the formula  $\mu - 1 = c/(n_0^2 - n^2)$ , in which  $c$  was  $9.43264 \times 10^{27}$  and  $n_0^2$   $17008.9 \times 10^{27}$ . Improvements in the source of light (use of the arc with poles of cadmium-silver and lithium-silver alloys) made it worth while to repeat the former measurements for the dispersion of the other rare gases, and the values of  $n_0^2$  now found agreed to within 2% with the former determinations. A table of the constants for the five rare gases is given.

F. S.

Molecular Dispersion of cyclopentadiene. A Correction. KARL AUWERS and FRITZ EISENLOHR (*Ber.*, 1910, 43, 1545. Compare this vol., ii, 367).—The theoretical value for the molecular dispersion of cyclopentadiene is 0.87 (not 0.46), and this agrees with the experimental value, so that the compound does not show exaltation.

J. J. S.

Wave-length Measurements in the Visible Region of the Arc Spectrum of Welsbach's Elements, Aldebaranium and Cassiopeium. JOSEF EDER and EDUARD VALENTA (*Zeitsch. anorg. Chem.*, 1910, 67, 102—106).—The two components of ytterbium, aldebaranium and cassiopeium, have been examined in the arc. Both elements give bright characteristic lines in the region from green to red, tables of which are given.

C. H. D.

Positive Band Spectrum of Nitrogen and its Variation with Temperature. ERNST ANGERER (*Ann. Physik*, 1910, [iv], 82, 549—576).—The spectra of the positive glow emitted by Geissler tubes containing nitrogen at the ordinary temperature and at the temperature of liquid air have been compared. Special arrangements were made to ensure that the conditions of discharge should be as nearly as possible the same at the two temperatures.

In general, the spectrum obtained at the lower temperature is much less intense than that emitted at the ordinary temperature. In the case of certain bands and lines, however, the lowering of temperature is not accompanied by any appreciable alteration in the intensity of the emitted light. Similar experiments with hydrogen and helium have shown that the spectrum of these gases is unaltered by change of temperature. On the other hand, argon appears to behave in the same way as nitrogen.

The wave-lengths of the nitrogen lines and bands are recorded in detail.

H. M. D.

**Dispersion in the Electrical Spectrum of Petroleum.** N. OROLENSKY (*Physikal. Zeitsch.*, 1910, 11, 433—440).—The dispersion in the electrical spectrum of Caucasian petroleum has been examined by the method used by Colley (*Abstr.*, 1908, ii, 909). Measurements of the refractive indices for electrical waves of different wave-lengths are recorded, and curves are drawn which show the dependence of the refractive index on the wave-length. These curves indicate the resistance of a large number of dispersion bands. The well-defined band between 332 and 335 mm. (half wave-length in air) is also found in the electrical spectrum of toluene and acetone, and its presence in the spectrum of petroleum containing naphthenes is considered to afford further evidence in favour of the view that this band is due to the methyl group.

With rise of temperature, this dispersion band appears to be displaced in the direction of greater wave-lengths. The variation of the refractive index of petroleum with temperature is only in approximate agreement with the requirements of the Clausius-Mossotti formula. H. M. D.

**Absorption Spectra of Nitrates.** KONRAD SCHAEFER (*Zeitsch. phys. Photochem.*, 1910, 8, 212—234, 257—287).—A detailed examination has been made of the absorption due to the  $\text{NO}_3$  group in metallic and organic nitrates. The experimental data show that these two series of compounds are sharply distinguished from one another by their absorption spectra. In the case of solutions of metallic nitrates, the absorption spectrum is almost independent of the nature of the metal and of the degree of ionisation of the salt. This specific character of the absorption is, moreover, not confined to solutions of the metallic salts, for it is found that solid potassium nitrate has the same spectrum as is shown by its dilute solutions.

The behaviour of organic nitrates is quite different. From the examination of methyl, ethyl, amyl, and allyl nitrates, it appears that the organic nitrates show only general absorption. Although these substances were examined under different conditions in the liquid and vapour form, and also dissolved in various solvents, there was no evidence of selective absorption. The observations are discussed from the point of view of the theories of Stark and Hantzsch. H. M. D.

**Absorption Spectra of Potassium Cobaltous Thiocyanate in Organic Solvents.** JAN VON ZAWIDSKI (*Chem. Zentr.*, 1910, i, 1426—1427; from *Chemik Polski*, 1910, 10, 49).—Potassium cobaltous thiocyanate,  $\text{K}_2\text{Co}(\text{CNS})_6$ , is soluble in many organic solvents, but not in hydrocarbons and alkyl halides. The solutions are dark blue, and the characteristic absorption spectrum is independent of the solvent. The solvents examined include alcohols, aldehydes, ketones, acids, nitrobenzene, esters, nitriles, cyanohydrins, and thiocyanates. The spectrum is therefore due to the complex  $\text{Co}(\text{CNS})_6$ , being independent of the ionising power of the solvent. The complex is broken up by water and formamide, and the pink colour of cobaltous is then obtained. C. H. D.

**Absorption Spectrum of the Three Xylenes in the Ultra-violet.** WILHELM MIES (*Zeitsch. wiss. Photochem.*, 1910, 8, 287—291. Compare Abstr., 1909, ii, 776).—In order to ascertain the influence of the relative position of the methyl groups on the ultra-violet absorption spectrum, the author has investigated the vapours of *o*- and *m*-xylene by the same method as that previously used for *p*-xylene. The absorption of *m*-xylene is considerably weaker than that of the *para*-compound, and contains only one series of bands instead of the two exhibited by *p*-xylene. The absorption of *o*-xylene is still smaller, and the photographs afford no evidence of any definite series of bands. In regard to the position of the heads of the bands, *p*-xylene approximates to *o*-xylene more closely than to the meta-compounds. The heads of the most intense bands are at the following wave-lengths; *para*  $\lambda = 2722.5$ , *meta*  $\lambda = 2721.5$ , and *ortho*  $\lambda = 2723$ . The relative behaviour of the three xylenes in the liquid state is similar to that found by the examination of the vapours.

H. M. D.

**Evidence of the Nature of Chemical Ring-compounds on the Basis of Ultra-violet Fluorescence.** HEINRICH LEY and W. GRÄBE (*Zeitsch. wiss. Photochem.*, 1910, 8, 294—300).—The fluorescence spectrum of  $\alpha$ -naphthylamine consists of a single broad band reaching from  $\lambda = 1920$  to  $\lambda = 2690$ . On addition of an equimolar quantity of hydrogen chloride to an alcoholic solution of the amine, the fluorescence band is reduced in intensity and displaced slightly towards the ultra-violet; at the same time a new band makes its appearance in the region  $\lambda = 2700$ —3100. With increasing relative proportions of acid, this band is resolved into a series of nine bands which closely resemble the fluorescence bands of naphthalene. These bands are attributed to  $\alpha$ -naphthylamine hydrochloride, and the close similarity between the spectrum of the hydrochloride and that of naphthalene is attributed to the existence of a similar condition in the ring structure of the two compounds. The entirely different fluorescent spectrum of the free base is attributed to the effect of the presence of the unsaturated nitrogen atom.

The absorption spectra of  $\alpha$ -naphthylamine and its hydrochloride are also quite different, but the latter resembles that of naphthalene.

H. M. D.

**Rotation Dispersion. I. Influence of the Solvent on the Rotation of Ethyl Tartrate and of Menthol.** HERMANN GROSSMANN (*Zeitsch. physikal. Chem.*, 1910, 73, 148—162. Compare Abstr., 1909, ii, 713; this vol., ii, 372).—The optical rotation of solutions of ethyl tartrate in a large number of solvents, including all the liquid halogen derivatives of methane and ethane, certain alcohols, benzene hydrocarbons, and a number of their derivatives, has been measured for light of different wave-lengths at 20°, and the results are represented graphically and also in tabular form. The magnitude of the rotation varies enormously with the nature of the solvent. In those solvents in which the specific rotation in the red is higher than that for the pure ester, the dispersion curve rises from red to blue, whilst for such solvents as tetrachloroethylene and tetrachloroethane



in which the specific rotation is less than that of the pure liquid, the dispersion curve falls from red to blue.

A progressive increase in the number of chlorine atoms in methane and ethane regularly lessens the specific rotation towards the right until the system becomes levorotatory, but beyond a certain point the rotation towards the right increases with an increase in the number of chlorine atoms.

The entrance of the nitro- and amino-groups into benzene greatly increases the rotation to the right in these solvents; the effect of the aldehyde and primary alcohol groups is also considerable, whilst other substituents, such as a single halogen or methyl group, have a slight diminishing effect.

In solvents which have only a slight effect on the specific rotation, the dispersion curve shows a maximum, as in the case of the ester itself. The greatest specific rotation was observed in pyridine, quinoline, and furfuraldehyde.

Measurements were made with 6, 15, and 30 grams of the ester in each solvent, and thus information has been gained as to the effect of change of concentration of the solvent on the rotation. In solvents in which the ester is strongly dextrorotatory, the specific rotation-temperature curve tends to fall as the concentration increases, whilst in levorotatory solutions it rises in the same circumstances. Quinoline and tetrachloroethane are exceptional, inasmuch as in the former case there are indications of a maximum, in the latter case of a minimum, in the rotation-concentration curve. For acetone a maximum, and for xylene and ethylene chloride minima, have actually been observed.

When menthol is used as optically active substance, change in concentration of the solvent has much less influence, and the course of the dispersion curves is very similar in all solvents. G. S.

**Chemical Effect of Ultra-violet Light on Gases. Oxidizing Actions. Combustion of Cyanogen and Ammonia; Synthesis of Formic Acid.** DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, 150, 1327—1329. Compare this vol., i, 349).—No paracyanogen is formed when cyanogen is exposed to ultra-violet light in presence of oxygen, the gas becoming completely oxidised to carbon dioxide and nitrogen. Under the same conditions, ammonia is first decomposed into its elements, the hydrogen then becoming oxidised to water; a mixture of hydrogen and oxygen, on the other hand, is unaffected by ultra-violet light.

On exposing a mixture of acetylene (1.60 c.c.) and oxygen (2.72 c.c.) for four hours at a distance of 4 cm. from a quartz-mercury lamp (220 volts), a mixture was obtained consisting of carbon dioxide (0.57 c.c.) and carbon monoxide (0.88 c.c.), together with formic acid, unaltered oxygen, and acetylene. A mixture of ethylene and oxygen in the same way gave carbon dioxide, formic acid, and carbon monoxide if the amount of oxygen was limited. W. O. W.

**Eder's Solution. II.** CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1910, 8, 197—211, 237—256. Compare Abstr., 1909, ii, 283; this vol., ii, 115).—Further experiments have been made relating to the

influence of iron and oxygen on the photochemical sensitiveness of Eder's solution. The sensitiveness is very largely dependent on the purity of the mercuric chloride and the ammonium oxalate which are used in the preparation of the solution. The active impurity is iron, and experiments with solutions containing very small quantities of ferric chloride show that the photochemical sensitiveness is proportional to the iron content. These observations lead to the conclusion that a solution of mercuric oxalate which is completely free from iron would not exhibit any photochemical effect.

Further measurements of the rate at which mercurous chloride is precipitated from an active solution show that the previously-observed period of induction corresponds with the time required for the disappearance of the free oxygen dissolved in the solution. With decreasing iron concentration, the retarding influence exerted by oxygen increases very rapidly. On account of this variable influence exerted by oxygen, the use of Eder's solution for exact actinometric measurements cannot be recommended.

Spectrophotographic observations show that Eder's solution has a specific absorption spectrum in the ultra-violet region. It is shown, however, that this spectral absorption is not necessarily accompanied by a special photochemical extinction.

H. M. D.

The Phosphorescence Produced by  $\alpha$ - and  $\beta$ -Rays. E. MARSDEN (*Proc. Roy. Soc.*, 1910, 83, 4, 548—561).—Continuous bombardment of a zinc sulphide screen by  $\alpha$ -particles produces a marked and rapid diminution of the luminosity, but only a slight reduction in the number of scintillations. The luminosity was diminished by rise of temperature (6% less at  $100^\circ$  than at  $15^\circ$ ), but no marked alteration occurred at solid carbon dioxide and liquid air temperatures. Infra-red radiation diminished the luminosity but slightly. Spectroscopic photographs of the luminosity showed a band toward the red, and another towards the blue end of the spectrum, and the intensity of the former decayed relatively to the latter with continued bombardment. An estimate of the fraction of the energy converted into light was effected by a differential air calorimeter, measurements being taken with the zinc sulphide covered with black paper and not covered. 1.5% of the total energy appeared as light energy. Willemite also underwent a reduction of luminosity with long bombardment, but not so rapidly as zinc sulphide, whereas the reduction in barium platinoeyanide was very rapid, falling to half value in eight minutes when exposed to  $5 \times 10^7$   $\alpha$ -particles per second per sq. cm. The phosphorescence of these materials under  $\beta$ -rays, and its decay after cessation of the exciting cause were also examined.

F. S.

Theory of the Luminosity Produced in Certain Substances by  $\alpha$ -Rays. ERNEST RUTHERFORD (*Proc. Roy. Soc.*, 1910, 83, 4, 561—572. Compare preceding abstract).—The theory proposed is that "active centres" exist in a substance rendered luminous by  $\alpha$ -rays uniformly distributed among the inactive molecules, and that a scintillation is the result of the dissociation of a number of these active centres lying in the path of the  $\alpha$ -particle, and that, after being

once struck, each active centre becomes ineffective in producing light. This explains the reduction of luminosity by bombardment, and the fact that the number of scintillations only slightly diminishes (Marsden). The experimental curves obtained are found to agree well with the theoretical curves worked out from this theory. According to it the diameter of the cylinder of material affected by the passage of a single  $\alpha$ -particle can be calculated from the observed curves of decrease of luminosity by continued bombardment, and it is shown that whereas for zinc sulphide and willemite the diameter is  $1.3$  and  $2.5$  ( $\times 10^{-7}$  cm.), which is somewhat larger than the diameter of a molecule, it is very much greater for barium platincyanide, namely,  $1.6 \times 10^{-5}$ . This excludes an earlier suggestion that the scintillations of zinc sulphide are due to the mechanical cleavage of small crystals.

F. S.

**Magnetic Line-Spectrum of  $\beta$ -Rays.** OTTO VON BAER and OTTO HAHN (*Physikal. Zeitsch.*, 1910, 11, 488—493).—If the  $\beta$ -rays which are exponentially absorbed are homogeneous, they should, after passage through two slits in a suitable magnetic field, be deviated uniformly, and give a sharp image of the slit when received on a photographic plate, as is well known to be the case for the  $\alpha$ -rays. If two or more homogeneous types are present, there should be received on the plate a magnetic line-spectrum consisting of two or more sharp images, the slower rays being the more easily deviated. In such a photograph taken with the active deposit of thorium, two sharp lines, due to the  $\beta$ -rays of thorium-A and thorium-D respectively, could be seen, and also three others, two due to very slow  $\beta$ -rays too feebly penetrating to be distinguishable from  $\alpha$ -rays in absorption measurements, and a third to rays slightly faster than those of thorium-A. For radium-E<sub>2</sub>, one not very sharp line only was observed. For mesothorium-2, a broad band, tailing off, due to slightly deviated  $\beta$ -rays, was seen, agreeing with an earlier view that the radiation is complex. In addition, four sharply separated lines due to very soft  $\beta$ -rays were observed. A radio-thorium preparation showed in addition to the lines due to thorium-A and thorium-D, another due to thorium-X, still more strongly deviated (compare following abstract). These results show that  $\beta$ -rays are expelled with definite and characteristic velocity like the  $\alpha$ -rays, and that probably each  $\beta$ -ray product emits only one group of typical  $\beta$ -rays.

F. S.

**A New  $\beta$ -Radiation from Thorium-X; Analogies in the Uranium and Thorium Series.** OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1910, 11, 493—497. Compare preceding abstract).—It is stated that a radium preparation has been obtained showing a gradual growth of radiation to double the maximum reached after a month, and this is regarded as evidence for the existence of a new product, radium-X, produced from radium and giving the soft  $\beta$ -rays ascribed to that substance, but no separation has yet been effected. From analogies between the uranium and thorium series, it was considered probable that thorium-X should give an absorbable  $\beta$ -radiation. In a series of experiments, thorium-X was freed as

completely as possible from thorium-A and thorium-B. The latter was removed by boiling the solution with charcoal, and the former by igniting the evaporated filtrate. A very feebly penetrating  $\beta$ -radiation always remained with the thorium-X so purified, and it was calculated that it was absorbed about three times as readily as the  $\beta$ -radiation of thorium-A. In the course of time, as thorium-A and thorium-B were regenerated, the  $\beta$ -rays showed a continuous rapid increase of penetration power. In conclusion, various analogies between the uranium and thorium disintegration series are elaborated.

F. S.

The Total Ionisation Produced in Different Gases by the Cathode Rays Ejected by X-Rays. R. D. KLEEMAN (*Proc. Roy. Soc.*, 1910, A, 84, 16-24).—The experiments were made to test whether, as appears probable, the energy necessary to make an ion from any given atom is independent of the nature of the ionising agent or of its penetrating power. The ionisations in various gases and vapours at low pressures produced by a beam of X-rays of known intensity were measured when screens of cardboard coated with gold leaf on one side were interposed in the path of the beam. By subtracting the effect when the gold-coated side was towards the ionisation chamber from that when the opposite was the case, the ionisation produced by the cathode radiations from the gold only could be found. Owing to the feeble penetrating power of these radiations, they are entirely absorbed in the gas, even at low pressure, and for gases containing atoms no heavier than oxygen, the ionisation was independent of the pressure. In heavier gases containing bromine and chlorine, the ionisation increased with pressure, which is considered to be due to the gold generating soft X-rays in addition, which are relatively much more readily absorbed by heavy gases. This could in most cases be corrected for. The results showed that the relative total ionisation produced by the cathode rays in different gases was similar to what Bragg had found for the same gases exposed to  $\alpha$ -rays. It is deduced from this that the energy necessary to ionise an atom is the same for the cathode ray as for the  $\alpha$ -ray, and that the path of the cathode ray in different gases is inversely as the sum of the square roots of the atomic weights of the constituent atoms of the molecule. A summary of other work bearing on the question of the total energy required to produce an ion is given at the end of the paper.

F. S.

On Secondary Homogeneous X-Radiation. J. C. CHAPMAN and S. H. PIPER (*Phil. Mag.*, 1910, [vi], 19, 897-903).—A primary beam of X-rays of a degree of hardness sufficient to excite homogeneous copper radiation without directly stimulating the homogeneous silver rays, produced only homogeneous copper radiation when caused to fall on a plate composed of an alloy of one part of copper to two parts of silver. The experiment points to the conclusion that the homogeneous radiations are not produced by the electrons ejected by the impact of X-rays from the atoms, but from the vibration of the atoms from which the electrons are ejected. An experiment to see

whether secondary  $X$ -radiation persisted, like phosphorescence, after the exciting cause ceased, gave negative results. From copper and zinc it cannot continue at  $\frac{1}{250}$ th of its initial strength  $\frac{1}{10000}$ th second after the exciting cause ceases. F. S.

**Radium- $D$  and its Products of Transformation.** GEORGE NICHLAEVICH ANTNOFF (*Phil. Mag.*, 1910, [vi], 10, 825—839).—The period of radium- $D$  has been determined by a new method, in which the number of  $\alpha$ -particles emitted from radium- $F$  produced after the lapse of a known time (120 to 320 days) from a known initial quantity of emanation, left to decay in a sealed tube, has been counted by the scintillation method. The mean of five results gives 16.5 years for the period of half-change with a probable accuracy of  $\pm 0.5$  year. The existence of two short-lived products (radium- $E_1$  and  $E_2$ ) between radium- $D$  and  $F$  has been disproved. Only one, radium- $E$ , exists, giving  $\beta$ -rays, with a half-period of five days. A piece of platinum foil was exposed to the emanation from 150 mg. of radium bromide for a day, and the active deposit dissolved off and evaporated in a watch-glass. A few hours after the exposure, it is practically pure radium- $D$ .  $\beta$ -Radiation, due to the formation of radium- $E$ , was generated regularly and normally with the five-day period. Radium- $E$  separated from radium- $D$  by precipitating the latter with barium sulphate decayed exponentially with the same period. In another method, radium- $D$  was volatilised from radium- $E$  in a blowpipe flame. The absorption of the  $\beta$ -rays of radium- $E$  is exponential, the value of the absorption-coefficient for aluminium being  $43(\text{cm.})^{-1}$ , and for copper,  $164(\text{cm.})^{-1}$ . From old solutions of radium, radium and radium- $D$  are completely removed by precipitation with barium sulphate, whereas radium- $E$  and radium- $F$  are left in the solution. F. S.

**The Estimation of Radium.** STEWART J. LLOYD (*J. Physical Chem.*, 1910, 14, 476—481).—The effect of the addition of various reagents on the measurement of the radium in a radium-barium solution by means of the usual emanation method has been investigated. Only in the presence of hydrochloric or nitric acids is the emanation fully evolved. Sulphuric acid and sodium carbonate, which precipitate the barium and radium, diminish the amount of emanation evolved very markedly. The production of other precipitates in the solution did not cause much effect. Stirring and heating the precipitate of barium sulphate after its formation facilitates greatly the subsequent evolution of emanation, due to the radium being released when the precipitate recrystallises. Some time after the precipitate of barium sulphate has been formed in a radium-containing solution, the latter again recovers its initial power of evolving emanation. F. S.

**The Constant of Uranium- $X$ .** FREDERICK SODNY and ALEXANDER S. RUSSELL (*Phil. Mag.*, 1910, [vi], 10, 847—851).—The decay curves of both the  $\beta$ - and  $\gamma$ -rays of the uranium- $X$  preparations from 45 kilograms of uranyl nitrate have been examined over a period of 230 days, in which time the radiation is reduced to 0.15% of the initial value. Both radiations were found to decay normally at exactly the

same rate, the value of the radioactive constant,  $\lambda$ , of uranium-X being  $0.0282(\text{day})^{-1}$ . The period of average life is 35.5 days, and of half-change, 24.6 days. The latter values are about 10% greater than those previously in use. Some of the preparations used showed a more rapid decay of the  $\beta$ -rays for the first ten days ( $\lambda = 0.033$  to  $0.029$ ), but the effect is ascribed to possible errors, such as absorption of moisture from the air. Both  $\beta$ - and  $\gamma$ -rays decay normally to zero. Some preparations were examined up to fourteen months from preparation, until the  $\beta$ -radiation was only  $\frac{1}{100,000}$ th of its initial value.

F. S.

**Rate of Decay of the Radioactivity of Polonium.** JOHN WILLIAM WATERS (*Phil. Mag.*, 1910, [vi], 19, 905—906).—The rate of decay of a specimen of polonium five years old, during which time the activity would be reduced to one-thousandth part of the initial, proved to be normal with a period of half-change of one hundred and forty-eight days. This is so near the rate found by Mme. Curie for freshly prepared material, that it is probable that the product of the change is not itself radioactive.

F. S.

**Table of Radioactive Elements.** HEINRICH GREINACHER (*Zeitsch. Elektrochem.*, 1910, 18, 267—269).—A table of the thirty known radioactive elements, containing the time in which their activity is halved, the kind of rays given out, the penetration and velocity of the  $\alpha$ -rays, and the absorption-coefficients of the  $\beta$ -rays for aluminium and of the  $\gamma$ -rays for lead.

T. E.

**Radioactivity of Minerale.** I. CORNELIO DOELTER and HEINRICH SIEK (*Monatsh.*, 1910, 31, 319).—Green zircons from Ceylon were found to be appreciably radioactive, but the red and brown varieties examined were not. A crystal of Norwegian monazite, not perfectly pure, was active, but it is probable that this mineral owes its activity to isomorphous inclusions of thorium phosphate. Barytes was found to be inactive. Some fluorites showed activity, others did not.

F. S.

**Radioactive Minerals in the Collection of the Wagner Free Institute of Science.** CARL BOYER and EDGAR T. WHERRY (*Trans. Wagner Inst. Sci. Philadelphia*, 1910, 7, 31).—Plates are given showing the relative activity to the photographic plate of many of the common radioactive minerals. In a table, the activity of sixteen minerals to the electroscope and to the photographic plate respectively are recorded.

F. S.

**Radioactive Minerale in Common Rocks.** JOHN W. WATERS (*Phil. Mag.*, 1910, [vi], 903—904. Compare *Abstr.*, 1909, ii, 848).—Dalbeattie granite yielded as its most radioactive constituent, allanite. Other heavy minerals present were magnetite, sphene, and apatite, which were but feebly radioactive.

In Mourne granite, similarly, the most active constituent was zircon containing small amounts of a titanium mineral, and in this

case the activity was sufficient to produce scintillations on a zinc sulphide screen. It was intended to use these minerals in the determination of the geological age of the specimen by means of the helium ratio, but owing to their size being of the same order as that of the range of the  $\alpha$ -ray in minerals (0.04 mm.), results so obtained would not be trustworthy.

F. S.

**Radioactivity of the Mineral Springs of the Tyrol. II.** MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1910, 31, 221—244).—Tables are given of the amounts of radium emanation, expressed in Mache units, in very numerous mineral springs and sources of common drinking water in the Tyrol. The presence of radium in some of the more active waters was proved by boiling out the emanation, and re-testing the water after it had been kept a long time in a tightly closed flask. In another table the radioactivity of numerous stones of the district, and of the sediments from the active springs, is given. The most active water and sediments are those of the Bad Froy at Villnösstal, the former showing an activity of from 30 to 40. The rock in the neighbourhood is described as a graphitic phyllite.

F. S.

**Ionisation of Air by the Carbon Monoxide Flame and by Radium Radiation. Mobilities of the Ions Present.** MAURICE DE BROGLIE (*Compt. rend.*, 1910, 150, 1425—1426).—The combustion of dry filtered carbon monoxide gives rise to ions of a totally different order of mobility from those produced by the moist gas.

Direct comparison of the ions produced in air by radium and by a dry carbon monoxide flame showed that the mobility of the positive ions is 20% greater, and of the negative ions 70% greater, in the case of radium. Having regard to the considerable experimental error, and to the presence of some carbon dioxide in the one case, the author draws the conclusion that the ions produced by the combustion of carbon monoxide and by radium have very similar mobilities and are probably identical.

R. J. C.

**Electrical Conductivity of Alloys and their Temperature-coefficients. III.** W. GUERTLER (*Physikal. Zeitsch.*, 1910, 11, 476—479. Compare Abstr., 1908, ii, 557).—Polemical against Rudolphi (Abstr., 1908, ii, 923).

H. M. D.

**Ionisation of Salts in Mixtures with no Common Ion.** MILES S. SHERRILL (*J. Amer. Chem. Soc.*, 1910, 32, 741—748).—Determinations have been made of the conductivity of solutions of mixtures of potassium chloride and sodium sulphate, and of sodium chloride and potassium sulphate. The measurements were made at 18°, and at concentrations of 0.2*N* and 0.1*N*. The results show that when the concentrations of the separate ions of the salts in the mixtures are calculated by the principle expressed by the equation:  $A(B)/A_xB_y = K(\Sigma i)^{2-n}$ , where  $\Sigma i$  is the total equivalent ion concentration, the sum of the ion concentrations is obtained with an accuracy of about 0.5% at 0.2*N*, and of about 0.25% at 0.1*N*.

E. G.

**Dielectric Cohesion of Neon and its Mixtures. Quantitative Analysis Based on Measurement of Dielectric Cohesion.** EDMOND BOUTY (*Compt. rend.*, 1910, 150, 1380—1383. Compare this vol., ii, 178).—The dielectric cohesion of neon is smaller than that of any other gas. By successive fractionations, the author has reduced the cohesion of neon to 6.1. Extrapolation gives 5.6 as the dielectric cohesion of absolutely pure neon, helium having cohesion 18.3 and hydrogen 205. A series of measurements on mixtures of neon and carbon dioxide (418) and of neon and air (419) shows that the resultant dielectric cohesion is very much higher than that calculated from the law of mixtures when the proportion of diatomic gas is small. The same formula expresses the effect of carbon dioxide and of air on neon when the proportion of neon is at least 97.5%. By means of this formula it is estimated that neon of dielectric cohesion 6.3 contains less than one-twentieth % of impurity, and the purest neon obtained (6.1) less than one-fiftieth % of impurity calculated as air.  
R. J. C.

**Potential of the Thallium Electrode.** GILBERT N. LEWIS and CARL L. VON ENDE (*J. Amer. Chem. Soc.*, 1910, 32, 732—741).—The value of the potential of the thallium electrode in solutions of thallous chloride and nitrate has been determined. It has been found that, contrary to the view of Neumann (*Abstr.*, 1894, ii, 373) and others, the electromotive behaviour of the thallous ion is in no way anomalous. Denham's statement (*Proc.*, 1908, 24, 76) that, in presence of the thallous ion, thallium forms sub-thallous ions could not be confirmed. Earlier measurements of the thallium potential were vitiated by the oxidation of the electrode and the consequent increase in thallous ion concentration. On taking precautions to avoid such oxidation, it has been found that Nernst's formula holds for the thallium electrode over a large range of concentration with greater accuracy than has been shown to be the case with any other electrode. The assumption of the validity of Nernst's formula and the solubility product rule leads to measurable errors when the concentration is as high as  $N/10$ , and the direction of these errors can be predicted.

The potential of thallium in saturated solutions of thallous chloride in  $N/10$ -potassium chloride, and in  $N$ -potassium chloride has been determined. The potential of thallium against the hypothetical normal thallous ion is 0.6170 volt at 25° when the normal calomel electrode is taken as zero. The value 0.602 volt found by Brislé (*Abstr.*, 1909, ii, 463) was obtained at about 17°. The difference between these values may be due to the difference in temperature, but if so, the thallium electrode must have an exceptionally high temperature-coefficient.  
E. G.

**Cathode Fall [of Potential] in Argon at a Potassium Electrode and its Diminution by the Photoelectric Effect** GEORGE GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1910, 12, 411—413. Compare Dember, *Abstr.*, 1906, ii, 516).—The author has measured the alteration of the cathode potential fall when a potassium electrode



illuminated by a mercury vapour quartz lamp. When the discharge tube was filled with argon at a pressure of 5 mm. of mercury and the current passing was such as to give a normal fall of potential, this was found to be reduced from 64 to 38.5 volts when the rays from the lamp were admitted to the electrode through a quartz window. By interposing a glass plate, 2 mm. thick, the fall of potential was reduced from 64 to 47 volts. When the current passing through the tube was increased so as to make the cathode potential fall abnormal, the effect of illuminating the electrode was exactly opposite, the potential difference being increased by 8—10 volts. H. M. D.

**Production of Negative Electricity during the Reaction of Gases on Base Metals.** FRITZ HABER and GERHARD JUST (*Zeitsch. Elektrochem.*, 1910, 16, 275—279).—An alloy of sodium and potassium is allowed to drop slowly from a tap funnel. The drops fall along the axis of a cylinder of platinum gauze, which is carefully insulated and connected to an electroscope. In an atmosphere of pure dry hydrogen or nitrogen, the potential of the platinum cylinder falls from 22½ to 21 volts in about four minutes, when it is positively charged, or in six and a-half minutes when the charge is negative. This is independent of whether the metal is dropping or not. When a trace of water vapour is admitted, the same fall of potential takes place in seven or eight seconds when the metal is dropping through the positively-charged cylinder, whilst with a negative charge the leak is the same as in dry gas. Hydrogen chloride, iodine vapour, and oxygen give much the same effect in water vapour. Thionyl chloride and carbonyl chloride give much greater effects; with the latter especially, the whole positive charge disappears almost instantaneously, whereas a negative charge is not affected. In every case in which the electrical action occurs, the bright surface of the drops is tarnished. The effect takes place in the dark, but is more marked in the light. It is attributed to the escape of some of the negative electrons in the metal during the chemical change. T. E.

**The Electromotive Properties of the Mercury Oxides.** ARTHUR JOHN ALLMAND (*Zeitsch. Elektrochem.*, 1910, 16, 254—263).—The potential difference between mercury and *N*- or 0.1*N*-solutions of sodium or potassium hydroxide containing mercuric oxide in excess is measured at 18°, the potential difference of the *N*-calomel electrode being taken as 0.283 volt. Twelve different samples of mercuric oxide (some yellow and some red) were used. In every case the initial potential difference falls gradually to a practically constant final value. It is shown that the differences are entirely due to differences in the size of the particles. The red and yellow modifications are identical, as both contain prisms and apparently quadratic plates; by prolonged shaking with a solution of potassium chloride, the smaller particles disappear, and the same potential difference is then obtained whether the initial substance is red or yellow. The final values obtained, at 18°, are: *N*-NaOH, +0.115 volt; *N*-KOH, +0.112 volt; *N*/10-NaOH or KOH, +0.168 volt. The electrode is recommended as a standard electrode.

From these results the author calculates that the normal potentials:  $\text{Hg}_2^{2+} \rightarrow 2\text{Hg}$  and  $\text{Hg}^{2+} \rightarrow \text{Hg}$  are +0.775 and +0.835 volt respectively. The solubility product of mercuric oxide at  $18^\circ$  is  $4 \times 10^{-26}$ , and its dissociation pressure is  $6 \times 10^{-22}$  atmosphere.

Mercurous oxide gave no definite potential difference; the values fell very quickly to those obtained with mercuric oxide.

T. E.

**High Sensibility Selenium Cells.** F. C. BROWN (*Physikal. Zeitsch.*, 1910, 11, 481—482).—The preparation of a form of selenium cell, highly sensitive to light, is described. The selenium was obtained by making a mixture of 10 parts of amorphous selenium and one part of the red, crystalline modification into a thick paste with ether, allowing the ether to evaporate at the ordinary temperature, and then heating the mixture for five hours at  $170^\circ$ . The amorphous selenium was prepared by precipitation of a potassium cyanide solution by means of hydrochloric acid; the crystalline form by exposure of a solution of amorphous selenium in carbon disulphide to the action of sunlight.

The electric conductivity of a selenium cell obtained in this way was found to increase three hundred times on exposure to light at  $3^\circ$ . With rise of temperature, the sensitiveness diminished, and at  $39^\circ$  the ratio of the conductivities was only 80.

H. M. D.

**New Photoelectric Property of Selenium.** F. C. BROWN (*Physikal. Zeitsch.*, 1910, 11, 482—483. Compare preceding abstract).—A new modification of selenium has been obtained, the electric conductivity of which is about a million times as large as the ordinary photoelectric variety. The method of preparation of this form of selenium is not described. It is, however, unstable, shows a slight diminution of conductivity on exposure to light, and the conductivity increases with rise of temperature.

H. M. D.

**Fuel Batteries.** ITZER TAITELBAUM (*Zeitsch. Elektrochem.*, 1910, 16, 286—300).—The Jaques cell was first studied. A layer of powdered quicklime was pressed into the bottom of an iron crucible, and an iron cylinder with a serrated lower edge was embedded in the lime. In this way the crucible is divided into two compartments separated by the quick-lime diaphragm. The whole is filled with fused sodium hydroxide, and a carbon electrode placed in the inner compartment. The crucible itself forms the positive electrode, and sodium manganate is dissolved in the outer compartment to serve as an oxygen carrier. The carbon electrode alone gives a very small current, but when fuels, such as sucrose, charcoal, coal or tallow, or gases, such as carbon monoxide, hydrogen or coal gas, are introduced into the inner compartment, considerably larger currents are obtained. The combustion of 0.1 gram of sugar in the cell, for example, yielded 1346 coulombs, instead of 1351 coulombs calculated for quadrivalent carbon. Other substances gave current efficiencies varying from 100% for charcoal to 24% with ordinary coal. The *E.M.F.* of the cell (at  $370$ — $390^\circ$ ) varies from 0.75 volt (sawdust) to 0.54 volt (carbon tube) on open circuit, but this falls when a current is taken from the cell; for example, with

0.15 ampere the *E.M.F.* is 0.44 volt with sawdust, and less than 0.1 volt with the carbon tube: the other substances tried gave intermediate values.

A cell was next investigated in which strong sulphuric acid was the electrolyte. The potential difference between platinum and sulphuric acid containing a reducing agent was first measured by combining this electrode with the mercurous sulphate-*N*-sulphuric acid electrode. The same fuels as before were tried at temperatures between 50° and 300°; they give curves running parallel to, and below, that given by sulphur dioxide. The potential of the electrode is due to the presence of sulphur dioxide, formed by the action of the fuel on the sulphuric acid. The main difficulty with the oxygen electrode was to find a substance which would absorb atmospheric oxygen sufficiently rapidly to depolarise the electrode. Ferrous and mercurous sulphates are unsatisfactory. A mixture of vanadyl sulphate and vanadic acid or of thallous and thallic sulphates dissolved in strong sulphuric acid gives good results at temperatures above 200°. At 250° the potential of platinum in either solution in equilibrium with air is 1.35 volts (referred to the normal hydrogen electrode). The combination of the vanadium electrode with the fuel electrode gives an *E.M.F.* which varies between 0.3 and 0.6 volt on open circuit at 250° according to the nature of the fuel used; substances which reduce sulphuric acid rapidly, such as partly carbonised sugar and acetylene, give the highest values and the smallest degree of polarisation when current is taken from the cell. The fuel electrode may be made of carbon, but the oxygen electrode must be of platinum or gold. T. E.

**Fuel Batteries.** EMIL BAUR (*Zeitsch. Elektrochem.*, 1910, 16, 300—302).—From the determinations of the dissociation of sulphuric acid and sulphur trioxide made by Bodenstein and Katayama (*Abstr.*, 1909, ii, 468) and a measurement of the vapour pressure of 96% sulphuric acid at 250°, the *E.M.F.* of the combination  $\text{SO}_2$  | sulphuric acid |  $\text{O}_2$  is calculated to be 0.37 volt at 250°. The higher values (0.5 to 0.6 volt) found by Taitelbaum (preceding abstract) are attributed to the nascent condition of the sulphur dioxide. The *E.M.F.* which should be produced by the reversible combustion of carbon to carbon dioxide is about 1 volt; hence Taitelbaum's cell yields some 50 or 60% of the free energy of the carbon. T. E.

**Silver-Nickel Thermo-element.** GEORG VON HEVESTY and E. WOLFF (*Physikal. Zeitsch.*, 1910, 11, 473—476).—An investigation of the behaviour of the silver-nickel thermo-element between -80° and +920° has shown that it is very suitable for the measurement of temperatures between these limits. The curve showing the connexion between the thermo-electric force and the temperature exhibits neither a neutral nor an inversion point; it cannot be represented by an equation of the second order. The temperature-coefficient of the thermo-electric force has a maximum value between 180° and 220°, and a minimum value at about 370°. Above 370° the temperature-coefficient increases with the temperature up to about 780°, and then remains constant. The minimum value of the temperature-coefficient at 370° is connected with a change in the nickel at this temperature.

The readings of the thermo-element are reproducible with considerable precision. In contact with air at 600° to 700°, the nickel becomes brittle in consequence of the action of oxygen on the metal, and higher values for the thermo-electric force are obtained. H. M. D.

**The Thermoelectricity of Alloys.** I. ERNST RUDOLFI (*Zeitsch. anorg. Chem.*, 1910, 67, 65—96).—The thermoelectric behaviour of a number of simple binary alloys, the constitution of which is known, has been examined. The alloys, with the exception of those containing silver and gold, were melted in glass tubes in an atmosphere of hydrogen, and drawn into glass tubes 1.5 mm. in diameter, coated internally, if necessary, with lamp-black. Gold and silver alloys were melted in porcelain crucibles in nitrogen, drawn into porcelain tubes, and afterwards drawn into wire. The thermo-electromotive force of the wires or rods was then measured against copper and against nickel, one junction being in ice and the other in a vessel of paraffin, heated by an outer paraffin-bath. After heating to 170—180°, readings were taken as the temperature fell, a compensation method being used.

The results are compared with previous determinations of the hardness and electrical conductivity (compare Kurnakoff and Schentschuschny, *Abstr.*, 1908, ii, 932). Alloys in which the two components crystallise in the pure state, without forming solid solutions, have a thermo-electric power proportional to the concentration (tin-cadmium, tin-zinc). If there is a slight formation of solid solutions, the line is broken at the limit of saturation of that solution (zinc-cadmium, lead-tin, bismuth-cadmium, lead-antimony). If the two metals form a continuous series of solid solutions, the curve has the U-shape of the conductivity curve (gold-silver, gold-copper, copper-nickel, platinum-palladium). The curves therefore have the same form as those of electrical conductivity (compare Haken, this vol., ii, 387). Solid solutions are the most suitable for the construction of thermopiles.

C. H. D.

**Electric Vacuum Furnace.** OTTO RUFF (*Ber.*, 1910, 43, 1564—1574).—An electric furnace is described which may be used either as a resistance or an arc furnace. It is so arranged that it can be filled with a gas other than air, and it may be worked at pressures varying from 3 mm. to one atmosphere. The electrodes are placed vertically, and when used as a resistance furnace the resistance consists of a carbon tube inside which a small carbon crucible is supported. Opposite the crucible there is a slit in the tube, and the wall of the furnace also contains a quartz window, so that the temperature may be taken by means of a Wanner pyrometer. Temperatures of 1000—2700° can readily be obtained in a few minutes, and the furnace will withstand temperatures of 2000—2200° for several hours. The power required varies from 200 amperes at 15 volts to 700 amperes at 41 volts. When the vacuum is satisfactory, the carbonising effect of the furnace atmosphere on the substance being heated is inappreciable.

Vanadium (96—97%) was readily obtained by the reduction

of vanadium trioxide with carbon. The following melting points were determined: platinum, 1745—1755°; molybdenum, 2110°; iridium, 2210—2225°; kaolin, 1912—1915°; tungsten (99.2%), 2575°. Titanium containing 5% of carbon could not be melted completely at 2700°.

The oxides of aluminium, magnesium, and calcium were found to be more volatile and fusible than hitherto supposed. At low pressures (5 mm.), and with small quantities of substance, they were completely volatile below the melting point. In nitrogen at atmospheric pressure, aluminium oxide had m. p. 2065°; the melting point of calcium oxide was in the neighbourhood of 2000°, but could not be exactly determined; magnesium oxide vaporised rapidly at 2100°, but the m. p. is certainly much lower than 2500° (compare Arndt, *Chem. Zeit.*, 1906, 30, 211). The furnace was so adapted that the electrical conductivity of these oxides could be measured, and it was found that there is a big increase in the conductivity when fusion takes place.

Silicon tetrafluoride is not acted on by carbon, even at the highest temperatures used.

T. S. P.

**Process of Rapidly Forming Lead-Accumulator Plates by means of Phosphoric Acid and Phosphates.** FRANZ FISCHER (*Zeitsch. Elektrochem.*, 1910, 16, 355—357).—The lead plate to be formed is placed between two others (1 cm. distant) in a 10% solution of disodium hydrogen phosphate at 80°. The applied *E.M.F.* is 2.2 volts, and it must never exceed 2.6 volts. After twenty-four to thirty-six hours, an adherent layer of lead monoxide is produced on the anode, which is readily reduced to lead, but is very slowly oxidised to peroxide. Lead phosphate is probably the initial product, and this is decomposed by the sodium hydroxide formed at the cathode; a diminution of volume occurs in the change, and the layer of oxide is therefore porous. The volume diminishes further when the oxide is reduced to lead, but increases when it is oxidised to peroxide, which explains the difference in the rates of these changes, the increase of volume filling up the pores and so confining the action to the surface.

The formation of the plate is therefore completed by reducing it in sulphuric acid of D 1.18 with 0.01 ampere per sq. cm., washing it free from phosphoric acid, and then charging it (as anode) in sulphuric acid of D 1.09 at the same current density until oxygen is evolved freely. The reduction requires the same time as the formation, and the oxidation twice as long. The whole operation occupies four or five days.

T. E.

**Electrolysis of Alkali Bromides and Retardation of the Anodic Separation of the Halogens.** FRITZ FOERSTER and J. YAMASAKI (*Zeitsch. Elektrochem.*, 1910, 16, 321—355).—A very extensive and accurate series of experiments is recorded on the electrolysis of sodium bromide. The influence of alkalis, concentration, temperature, rate of stirring, current density, and platinising the anode are studied in detail. The results are in complete agreement with the theory of the process given by Kretschmar (*Abstr.*, 1904, ii, 814).

At platinum anodes, bromine is liberated at the reversible bromine potential only when the anode is quite free from oxygen. When the platinum contains oxygen, a higher potential is required. The excess potential required is especially large at smooth platinum surfaces and in alkaline solutions. Similar effects have been observed with chlorine and oxygen itself, and they are doubtless due, as Luther and Brisee suppose (Abstr., 1903, ii, 708), to the formation of compounds of platinum and oxygen on the surface of the anode.

T. E.

**Electrolytic Formation of Films of Zinc on the Surface of Liquids.** HERBERT FREUNDLICH and W. NOVIKOW (*Zeitsch. Elektrochem.*, 1910, 16, 394—400).—The formation of floating films of zinc studied by Mylius and Fromm (Abstr., 1894, ii, 267) is again investigated. The formation of the film only occurs in an atmosphere containing oxygen (at least 1% mixed with nitrogen, carbon dioxide, or hydrogen), and the surface of the zinc sulphate solution must be covered by a film of some liquid which does not mix with it. Oxidation of the zinc is of secondary importance, but the formation of the film depends on the primary separation of zinc sponge (amorphous zinc) which is favoured by oxygen. The nature of the zinc sponge is uncertain; it always contains oxide, which remains undissolved when the current is reversed. The presence of small quantities of ammonium salts, salts of amines, tartaric acid, citric acid, and potassium cyanide in the 50% zinc sulphate solution prevents the formation of the film. The ammonium salts are the most active: 0.0005 mol. of ammonium sulphate to 1 mol. of zinc sulphate is sufficient. The action is apparently due to an acceleration of the change of amorphous into crystalline zinc. A thin layer of almost any liquid which does not mix with the zinc sulphate solution or of any solid (so long as it remains pasty) brings about the film formation. The thickness of layer necessary is found to be from 0.5 to  $2\mu$ .

T. E.

**Theory of Electrolytic Ions. IV. Coincidence of the Diameter of Atoms and of Ions not Related to the Solvent.** RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1910, 73, 252—255).—Compare Abstr., 1909, ii, 541).—The diameters of a number of univalent elementary ions have been calculated from the ionic mobilities by Einstein's formula, which at  $18^\circ$  reduces to  $\mu_{18} = 1/\rho \cdot 7.562 \times 10^{-7}$ , where  $\mu_{18}$  is the ionic mobility at  $18^\circ$ , expressed in the usual units, and  $\rho$  is the radius of the ion. The results are compared with the diameters of the respective atoms, calculated by Reinganum's formula (compare Rappenecker, this vol., ii, 590),  $\sigma = 2\rho = 0.882 \cdot 10^{-8} \sqrt{m/d}$  cms., in which  $\sigma$  is the molecular diameter,  $m$  the molecular weight, and  $d$  the density of the substance in the liquid state at its boiling point, and it is shown that the diameter of the ions is of the same order as that of the free atoms ( $2.6 \times 10^{-8}$  cm.), with the exception of lithium, for which the ionic diameter is more than double that of the atom. It follows that the ions in general cannot be highly hydrated; they may, however, be associated with three or four molecules of water. The lithium ion is hydrated to a considerable extent.

This does not apply to ions related to the solvent, the diameters of the hydrogen and oxygen atoms being three to four times those of the ions, as calculated from the ionic velocities.

G. S.

**The Relation between the Formation of Nitric Oxide and the Electrical and Thermal Properties of Short Direct Current Arcs with a Cooled Anode.** WILHELM HOLWEGG (*Zeitsch. Elektrochem.*, 1910, 16, 369—390).—The combustion of atmospheric nitrogen in a short arc formed between a water-cooled silver anode and a heated cathode was studied. The cathode was a strip of iridium foil, coated with lime, and heated by an independent current to a temperature not far short of its melting point. The arcs studied were from 0.8 to 4 mm. long; the current was varied from 0.07 to 0.2 ampere, and the voltage required lay between 90 and 300 volts.

The highest concentrations of nitric oxide were obtained with stationary gas, the shortest arc (1 mm.), and 500—600 mm. pressure in these circumstances over 9% of nitric oxide was obtained, using air. The yield (of nitric acid) was 70 to 80 grams per kilowatt-hour and this was almost independent of the length of the arc.

A careful study of the electrical properties of the arc showed that the anode and cathode falls of potential take place just at the surface of the electrodes; the distance through which they extend was too small to be measured; the fall of potential along the arc was quite constant. The falls of potential at the electrodes therefore have no influence on the formation of nitric oxide; they do not even effect the temperature of the electrodes, the one being cooled and the other heated independently of the current in the arc. The formation of nitric oxide is therefore entirely controlled by the fall of potential along the arc and the current flowing. The fall of potential varied from 100 to 200 volts per cm., whilst in the long arcs used in manufacturing practice it is under 10 volts per cm.

The temperature of the short arcs is lowest near the cooled anode and it increases with the pressure of the air. A very fine platinum wire placed in the arc quite close to the anode did not melt when the pressure was 1 atmosphere; at 100 mm. pressure it could be moved 3 or 4 mm. away from the anode before it melted. The very fine iridium point which was plugged into the arc in order to measure the fall of potential along it never showed the slightest indication of fusion, and the temperature of the iridium cathode which was at the hottest end of the arc could not exceed the melting point of iridium without stopping the experiment. It is therefore regarded as certain that the temperature of the arc nowhere exceeded 3000° absolute, at which temperature the purely thermal equilibrium between oxygen, nitrogen, and nitric oxide corresponds with about 4% of nitric oxide in the mixture. The formation of nitric oxide in these experiments is therefore due to collisions of ions, whereas in the low tension arcs employed in practice it is probably a thermal phenomenon. T. E.

**Magnetisation of Liquid and Solid Oxygen.** H. KAMBERLING OMPES and ALBERT PERRIER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 799—835).—Measurements have been made of the magnet

susceptibility of liquid and solid oxygen. Between  $-183^{\circ}$  and  $-208^{\circ}$  the specific susceptibility of liquid oxygen is inversely proportional to the absolute temperature, and can be represented by the equation:  $\chi = 0.002284/\sqrt{T}$ . The variation of the susceptibility of solid oxygen with temperature is exactly similar, and can be represented by  $\chi = 0.001690/\sqrt{T}$ , which holds between  $-259^{\circ}$  and the melting point of oxygen. The two equations indicate that the susceptibility of liquid oxygen at its freezing point is 1.3 times as great as that of the solid form.

It is probable that the observed variation of the magnetic susceptibility with the temperature gradually changes its form as the temperature rises, and that at higher temperatures the variation is in agreement with Curie's law, according to which the susceptibility is inversely as the absolute temperature. H. M. D.

**The Magnetic Properties of the Modifications of Iron.** SIEGFRIED HILPERT (*Zeitsch. Elektrochem.*, 1910, 16, 390—394).—A theoretical discussion. Between  $700^{\circ}$  and  $760^{\circ}$  iron becomes practically non-magnetic, and its specific heat exhibits anomalies. These phenomena are usually ascribed to the formation of  $\beta$ -iron. The author thinks that the anomalous specific heat may be due to the breaking up of the polar arrangement of the magnetic molecules by their more energetic vibration at high temperatures. This would absorb energy, and so explain both the disappearance of the magnetism and the anomalous specific heat without the assumption of a new modification of iron.

$\gamma$ -Iron is also supposed to be magnetic at low temperatures, and to lose its magnetism at high temperatures in the same way as  $\alpha$ -iron. This explains why steels containing martensite are readily magnetised. T. E.

**Influence of the Magnetic Field on the Passive State of Iron.** HORACE G. BYERS and MARC DARRIN (*J. Amer. Chem. Soc.*, 1910, 32, 750—756).—It has been shown by Byers (Abstr., 1908, ii, 1026) that when iron is used as an anode in various electrolytes, it can be rendered passive by a definite current density. Nichols (Abstr., 1886, 668) has found that the passive state of iron in nitric acid can be destroyed by placing the metal in a strong magnetic field. It was therefore considered of interest to ascertain whether the passive state of iron used as an anode would be similarly affected by the magnetic field.

As a result of experiments, it was found that the passive state could not be destroyed by any magnetic field producible with the apparatus available. It is shown that in solutions of nitric, sulphuric, and phosphoric acids, and also of nitrates and sulphates, the transition point of passive to active iron is a function of current density, and that the transition is retarded by the magnetic field. It is suggested that passivity is the result of an altered state of the metal itself, and that the altered state may be analogous to that of a number of magnets, the negative poles of which are all presented to the electrolyte, the orientation being produced by the various agents which cause the passive state. E. G.



**Magnetic Analysis of Certain Chromophoric Groups.** PAUL PASCAL (*Compt. rend.*, 1910, 150, 1167—1169. Compare this vol., ii, 100).—The molecular susceptibility of an organic substance is composed of two factors ( $A + B$ ).  $A$  is the sum of the separate susceptibilities of the atoms, and  $B$  consists of a series of corrections for structural peculiarities, such as double linkings, etc. The quantities  $B$  comprise a considerable part of the whole susceptibility, so that tautomeric changes of structure may give rise to very appreciable differences in susceptibility.

Aminoazobenzene, aminoazotoluene, and chrysoidine have susceptibilities almost identical with those calculated for the azo-structure. Hydroxyazobenzene, methoxyazobenzene, and benzeneazo- $\beta$ -naphthol are mixtures of the azo- and quinone forms.

$p$ -Azoanisole and  $p$ -azophenetole exist in two forms. The colourless form has a susceptibility corresponding with the azo-formula, whilst the red form, which is obtained on heating, has the much lower susceptibility of the quinonoid structure. Crystals of  $p$ -azoanisole of all gradations of colour, from colourless to red, can be obtained, giving corresponding intermediate values of the susceptibility.

Aurine appears to have the quinonoid structure, whereas magenta and other amino-derivatives of triphenylmethane are enolic.

The colourless form of the silver salt of 2:4:6-tribromophenol is a normal phenoxide, whereas the red form is quinonoid. R. J. C.

**Relation between the Specific Heats of Solid Substances and Temperature.** ALFRED MAGNUS and F. A. LINDEMANN (*Zeitsch. Elektrochem.*, 1910, 16, 269—272).—From Planck's theory of radiation, Einstein (*Ann. Physik*, 1907, 22, 180) has obtained an expression for the atomic heat of an element at constant volume:  $C = 3Rn\{e^4 A^2 / (e^4 - 1)^2\}$ , where  $A = \beta\nu/T$ ,  $n$  is the number of atoms in a molecule,  $\beta$  a constant ( $4.86 \times 10^{-11}$ ), and  $\nu$  is the frequency of vibration of the atoms. The authors find that by adding an empirical member,  $aT^{3/2}$ , to the expression, the specific heats at constant pressure, as they are always measured, may be represented with considerable accuracy. For the metals,  $n$  can be taken as unity; for the metalloids this gives a considerably less satisfactory agreement. The frequencies of the elements are in the same order as the values of  $\sqrt{S/V}A$  ( $S$  = melting point,  $V$  = atomic volume,  $A$  = atomic weight). The values calculated are:

	$\nu \times 10^{-12}$	$3\sqrt{S/V}A$	$a \times 10^6$		$\nu \times 10^{-12}$	$3\sqrt{S/V}A$	$a \times 10^6$
Bi	small	1.1	5.1	Cu	5.3	5.2	3.8
Pb	1.2	1.2	7.8	Al	6.8	5.6	5.2
Sn	2.7	1.5	10.5	Cr	7.2	6.4	5.6
Cd	2.7	1.9	6.8	I	2.7	1.0	15.5
Sb	3.1	1.9	4.2	S	5.5	2.6	—
Pt	3.1	3.2	6.3	Si	10.7	6.7	—
Ag	3.3	3.2	4.8	Graphite	22.6	> 21.0	—
Zn	3.7	3.2	6.1	Diamond	27.3	> 26.0	—
Mg	5.1	4.9	6.5				

T. E.

**Calculation of Electromotive Forces from Thermal Measurements.** ALFRED MAGNUS (*Zeitsch. Elektrochem.*, 1910, 16, 273—275).—The free energy of the reaction  $\text{Pb} + 2\text{AgCl} = \text{PbCl}_2 + 2\text{Ag}$  has been measured accurately by Broenstedt, and compared with Nernst's theorem by Halla (Abstr., 1908, ii, 755). The specific heats of the reacting substances are now more accurately known; the measurements are well represented by the formula obtained by Magnus and Lindemann (preceding abstract), using the following constants:

	<i>B<sub>γ</sub></i>	$\alpha \times 10^3$
Lead .....	58	7.8
Silver chloride .....	163	22.0
Lead     " .....	172	18.0
Silver .....	162	4.8

The only marked difference is in the case of Dewar's determination of the specific heat of lead between the boiling points of air and hydrogen. From the specific heats, the relation between the heat of the reaction and the temperature is obtained, and this makes it possible to calculate the free energy from the equation:  $A = -T \int Q/T dT$ , which follows from Nernst's theorem. The largest difference between the free energy calculated and that found is 0.2%. T. E.

**Energy Changes in Binary Systems. I. Confirmation of the Existence of the Compound Phenol-aniline in the Liquid State.** ROBERT KREMANN (*Monatsh.*, 1910, 31, 203—209. Compare Kremann and Ehrlich, Abstr., 1907, ii, 747).—The specific heats of the system phenol-aniline have been determined at different temperatures above the m. p. The method adopted was to raise 20 grams of an equimolecular mixture of aniline and phenol, sealed in a glass vessel, to the required temperature, and then to transfer quickly to a water calorimeter. Details of the corrections made are given. The sp. heat for the interval 99.0—74.9° is 0.376, which is the true specific heat for the equimolecular mixture of aniline and phenol; the value obtained for the interval 90—33.7° is 0.407, and the difference between the two values, namely,  $0.031 \times 65.7 \text{ cal.} = 2 \text{ cal.}$ , is the value for the heat of formation of the compound between the temperatures 33.7° and 99°.

The heats of admixture of equivalent quantities of aniline and phenol at different temperature intervals have been determined, and as expected, the observed heats diminished with rise in temperature. These observed heats are the actual heats of admixture plus the heat of formation of the additive compound, if such is formed. Since, however, with increase in temperature there is a tendency for the additive compound to dissociate, it follows that the amount of additive compound present diminishes with rise in temperature, and the observed heats of admixture must also diminish. The value found is about 1 calorie for an increase of 35.7°. J. J. S.

**Cryoscopic Determinations at Low Temperatures (−40° to −117°).** ERNST BECKMANN and PERCY WAENTIG [with M. NIESCHER] (*Zeitsch. anorg. Chem.*, 1910, 67, 17—61).—Pentane thermometers are

not satisfactory for work at low temperatures, on account of the viscosity of the pentane, the deposition of solid at very low temperatures, and the varying solubility of the gas used for filling. The platinum resistance thermometer, having the platinum wire wound on quartz or Jena glass, gives perfectly satisfactory results. The pattern used has a resistance of 25.3 ohms at 0°. One millimetre on the scale of the Wheatstone bridge, with the arrangement adopted, corresponds with 0.0017°.

The freezing apparatus has been already described (Bockmann, Junker, and Klopfer, *Abstr.*, 1909, ii, 137). A bath of light petroleum, cooled by a spiral containing liquid air, is used.

The following cryoscopic constants have been obtained: carbon tetrachloride 298, pyridine 49.7, chloroform 46.8, ethyl ether 17.9, hydrogen iodide 202.6, hydrogen bromide 94.1, hydrogen chloride 49.8, hydrogen sulphide 38.3. Toluene and cymene are suitable substances for determining the constants.

Chloroform and carbon tetrachloride resemble benzene in their very small dissociating power. Alcohols, dissolved in them, give high values for the molecular weight. The halogen hydrides have also only a small dissociating power, and compounds containing hydroxyl show association when dissolved in them. The conductivity of the solvent increases from hydrogen iodide to hydrogen bromide. In the solutions, a higher conductivity often accompanies a higher molecular weight (compare Steele, McIntosh, and Archibald, *Abstr.*, 1905, ii, 222). Benzophenone exhibits association and conductivity, increasing with the concentration, in hydrogen iodide, becoming successively less in hydrogen bromide and chloride. Acetone is associated in hydrogen iodide, corresponding with the compound,  $2C_6H_5O.HI$ , found by McIntosh and Archibald, (*Trans.*, 1904, 85, 919). Iodine is similarly associated in pyridine. Ethyl acetoacetate is not associated in chloroform.

Water does not dissolve in liquid hydrogen chloride, but dry ammonia at once forms ammonium chloride. Liquid hydrogen sulphide, which blackens white lead, but is without action on silver, has little dissociating power. Compounds containing hydroxyl are slightly associated in it. Benzophenone appears to be dissociated in dilute solution in hydrogen sulphide, but no electrical conductivity is detected.

The latent heats of fusion of the solvents used are calculated, and the desirability of determinations of the dielectric constants at low temperatures is pointed out. The methods of preparation of the liquefied hydrogen halides and sulphide are described. C. H. D.

**Properties of Iodine as a Cryoscopic Solvent.** F. OLIVARI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 488—489).—The author corrects certain of the results given in his previous paper (this vol., ii, 18).

Lead iodide cannot be employed as a solute for determining the molecular freezing-point depression of iodine, as it is insoluble in this solvent. For oxygenated organic compounds, as well as for the hydrocarbons and their halogen derivatives, the molecular weights in iodine solution are normal at very great dilutions. With potassium

iodide, the molecular weight appears to be approximately normal for very dilute solutions, increase of the concentration being accompanied first by increase, and later by decrease of the molecular weight.

T. H. P.

**Vaporisation. IV. HANNS VON JÜPTNER** (*Zeitsch. physikal. Chem.*, 1910, 73, 173—191. Compare Abstr., 1909, ii, 21).—By a combination of Mendeléeff's expansion modulus for liquids with some well-known rules referring to the relationships of the volumes of liquids and their saturated vapours, it is shown (1) that the temperature-coefficient of the density and the thermal expansion-coefficient have opposite signs; (2) the magnitude of both is the smaller the higher the critical temperature; (3) up to  $T = 0.7T_k$ , the temperature-coefficient of the density remains constant, whilst the expansion-coefficient increases with the temperature.

For low temperatures the ratio of the density,  $D_t$ , of the liquid at the temperature,  $T$ , to the critical density can be calculated by the simple expression:  $D_t/D_k = 4(1 - T/2T_k) = 2(2 - \theta)$ , where  $\theta = T/T_k$ , but at higher temperatures the more complicated expression:  $D_t/D_k = 2 - \theta - 2\sqrt[3]{1 - \theta} - \alpha\sqrt[3]{1 - \theta}^2$  is used, and for the ratio of the density of the vapour  $D_v$  to the critical density the corresponding expression:  $D_v/D_k = 2 - \theta - 2\sqrt[3]{1 - \theta} + \alpha\sqrt[3]{1 - \theta}^2$ . The expressions are tested by comparing the calculated and observed data for fluorobenzene and for ammonia, and the agreement, especially for the two latter formulae, is excellent;  $\alpha$  is a constant, and for fluorobenzene is 0.194, for ammonia, 0.1. A slight modification of the first formula,  $D_t/D_k = 2 + 1.87(1 - \theta)$ , is shown to give very good results up to  $T = 0.65T_k$ .

From the above equations, formulae are derived which admit of the calculation of the volumes of the liquid at different temperatures.

G. S.

**Vapour Pressures of Binary Mixtures. JOHANNES J. VAN LAAR** (*Zeitsch. physikal. Chem.*, 1910, 72, 723—751).—The author adversely criticises the recent work of Dolczalek (Abstr., 1909, ii, 22; this vol., ii, 184), who has applied the laws of dilute solutions to certain binary systems, and also the mathematical treatment of the partial pressures of binary mixtures by Story (compare this vol., ii, 184) and others, and points out that a satisfactory theoretical treatment is only possible on the lines laid down by van der Waals and by himself. The most important point is that the attraction factor  $a$  must be taken into account. All the possible types of vapour pressure curves for binary mixtures are discussed mathematically.

G. S.

**Fractionating Arrangement. ARNOLD HAHN** (*Ber.*, 1910, 43, 1725—1727).—The ordinary fractionating column possesses the disadvantage that the separate fractions all pass through the same side-tube. The arrangement described consists of a bulb tube with a ground-glass neck, into which fits a ground-glass stopper carrying the thermometer. Into the neck of the bulb tube are fused three side-tubes, each of which is connected with a receiver. The glass stopper

contains one hole, which can be placed opposite to each of the side-tubes in succession, the other two being meanwhile closed.

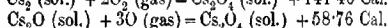
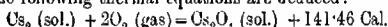
When used for distillations under diminished pressure, the three receivers are connected to a 4-way tube leading to the pump, but although all the receivers are evacuated at the same time, only one is in direct connexion with the distilling flask at any particular moment; consequently, there is no contamination of one fraction by vapours derived from other fractions.

T. S. P.

**Calibration and Manipulation of the Calorimetric Bomb.** WALTER A. ROTH (*Annalen*, 1910, 373, 249—266).—A less elaborate method than Fischer and Wrede's electrical process of calibrating a calorimetric bomb is described in detail, the necessary corrections being carefully explained. The bomb is Hugershoff's Precision Model; the calorimetric thermometer is a Beckmann thermometer, by means of which  $1/2000^\circ$  can be estimated. The results are accurate to within 0.1%. The trustworthiness of the method is proved by determining the total water equivalent of the calorimetric apparatus by exploding sucrose, benzoic acid, and naphthalene; taking the heats of combustion per gram of these substances as 3952.0 cal., 6325.4 cal., and 9640.5 cal. respectively, the water equivalent is found to be  $2623.3 \pm 0.6$  cal.,  $2623.4 \pm 0.8$  cal., and  $2622.5 \pm 0.7$  cal. The calibration is controlled by a fourth process, in which a known quantity of heat is generated electrically within the bomb; the water equivalent in this case is  $2623.1 \pm 1.0$  cal.

C. S.

**Heat of Formation of Cæsium Peroxide.** ROBERT DE FORCRAND (*Compt. rend.*, 1910, 150, 1399—1402. Compare Abstr., 1906, ii, 445).—The heat of dissolution of 1 gram-molecule of cæsium peroxide,  $\text{Cs}_2\text{O}_2$ , in an equivalent of 2% sulphuric acid is 33.02 Cal., from which the following thermal equations are deduced:



The heat of complete oxidation of cæsium (+141.46 Cal.) is very near that of complete oxidation of lithium ( $\text{Li}_2\text{O}$ , +143.32 Cal.), and the oxidation of strontium to monoxide ( $\text{SrO}$ , +138.64 Cal.), but is less than the heat of complete oxidation of strontium ( $\text{SrO}_2$ , +151.71 Cal.). The first oxygen atom combining with  $\text{Cs}_2$  gives +82.70 Cal., whereas the average for the next three atoms is +19.59 Cal. each. In the case of the sodium oxides,  $\text{Na}_2\text{O}$  and  $\text{Na}_2\text{O}_2$  are stable, whereas  $\text{Na}_2\text{O}_3$  and  $\text{Na}_2\text{O}_4$  are completely dissociated under ordinary conditions. It is argued by analogy that the 58.76 Cal. evolved in passing from  $\text{Cs}_2\text{O}$  to  $\text{Cs}_2\text{O}_2$  should not be distributed among the successive oxygen atoms equally, but in a decreasing ratio. Supposing that the temperature of dissociation of  $\text{Cs}_2\text{O}_3$  to  $\text{Cs}_2\text{O}_2 + \text{O}$  is about  $550^\circ$ , the heat of addition of the last oxygen atom would be about 12.5 Cal. The author suggests that the addition of oxygen atoms to  $\text{Cs}_2\text{O}$  liberates 28.26, 18.0, 12.5 Cal. successively.

The heat of formation of  $\text{Cs}_2\text{O}_4$  from  $\text{Cs}_2\text{O}$  is practically as great as the heat of hydration of  $\text{Cs}_2\text{O}$  to  $2\text{CsOH}$  (60.01 Cal.). At  $300^\circ$

to  $400^{\circ}$ , the order of these two values is reversed, so that on heating cesium hydroxide in oxygen, cesium peroxide would be exothermally produced with evolution of steam. Owing to the silver boats being attacked, pure cesium peroxide cannot be obtained in this way.

R. J. C.

**Heat of Formation of the Oxides of Molybdenum, Selenium, and Tellurium; Heat of Combination of Acidic Oxides with Sodium Oxide.** WILLIAM G. MIXTER (*Amer. J. Sci.*, 1910, [iv], 29, 488—496. Compare Abstr., 1909, ii, 865).—The heats of formation of the oxides and sodium salts have been calculated from the thermal data obtained by oxidising the elements or lower oxides by means of sodium peroxide. The following results are given:  $\text{Mo} + 3\text{O} = \text{MoO}_3$ , +181.5 Cal.;  $\text{Na}_2\text{O} + \text{MoO}_3 = \text{Na}_2\text{MoO}_4$ , +81.9 Cal.;  $\text{Mo} + 2\text{O} = \text{MoO}_2$ , +142.8 Cal.;  $\text{Se} + 3\text{O} = \text{SeO}_3$ , +48.8 Cal.;  $\text{Na}_2\text{O} + \text{SeO}_3 = \text{Na}_2\text{SeO}_4$ , +105.3 Cal.;  $\text{Te} + 3\text{O} = \text{TeO}_3$ , +83.6 Cal.;  $\text{Na}_2\text{O} + \text{TeO}_3 = \text{Na}_2\text{TeO}_4$ , +124.3 Cal.;  $\text{Te} + \text{O}_2 = \text{TeO}_2$ , +87.1 Cal. According to the heats of formation of the two oxides of tellurium, the conversion of the dioxide into the trioxide is an endothermic reaction.

H. M. D.

**Heat of Combination of Hydrogen Bromide with some Ethylenic Compounds.** WLADIMIR LUGININ and GEORGES DUPONT (*Compt rend.*, 1910, 150, 1346—1348. Compare Berthelot, Abstr., 1876, i, 870).—Berthelot's determinations of the amount of heat developed on the addition of halogen acids to unsaturated compounds are untrustworthy, owing to the small amount of the substances entering into combination in aqueous solution. More accurate results have been obtained by utilising xylene as the solvent; the heat of dissolution ( $Q$ ) of one gram-molecule of hydrogen bromide in this substance is given by  $Q = 6.344 - 51,000x + 188,000x^2$ , where  $x$  is the number of gram-molecules of acid in 100 grams of solution. The following values have been obtained for the addition of one gram-molecule of gaseous hydrogen bromide to one gram-molecule of the substance dissolved in xylene. Styrene, 16,653 cal.; octylene, 16,481 cal.; amylene, 17,614 cal.;  $\beta$ -methyl- $\Delta^2$ -pentylene, 19,008 cal.; cyclohexene, 16,292 cal.; pulegone, 16,910 cal. As the compounds examined and their additive products are liquid, the above numbers are practically identical with the heats of formation of the halogen derivatives.

W. O. W.

**Thermochemical Investigations. I. Relation between the Constitution and the Heat of Combustion of Unsaturated Compounds.** KARL AUWERS and WALTER A. ROTH (*Annalen*, 1910, 373, 239—248).—Very little is known regarding the relations between the constitutions of organic compounds and their heats of combustion. The more labile of two isomeric compounds has the greater heat of combustion, but even in unusually favourable cases the difference does not exceed 2%. Hence, any thermochemical method of investigation must be accurate to within 0.1—0.2%. Such accuracy has been attained by several investigators by means of the calorimetric

bomb, but unfortunately their results have not been hitherto certainly comparable. Fischer and Wrede (Abstr., 1909, ii, 165), however, have described a method whereby calorimetric bombs may be calibrated with an accuracy of 0.05%, so that it should now be possible to make the results obtained by different workers strictly comparable.

The authors commence their researches with an investigation of the heats of combustion of unsaturated compounds, particularly of those containing conjugate linkings. Stohmann and Langbein already have shown that the heats of combustion of propenyl compounds are about 0.5 to 0.8% greater than those of the less labile isomeric allyl compounds. Also, Thiele states that the system  $C:C:C:C:CH_2$  is more saturated than the system  $C:C:CH_2:C:C$ , and therefore has a smaller

heat of combustion. Further, it is known that the heats of combustion of  $\alpha\beta$ -unsaturated acids are smaller than those of  $\beta\gamma$ -unsaturated acids. Hence it seems that the nearer a pair of doubly linked atoms are together, the smaller the heat of combustion. This statement is supported by references to the heats of combustion of hexoic, hydrosorbic, and sorbic acids, of diphenyl, diphenylmethane, and dihenzyl, and of *m*-toluic and phenylacetic acids.

The authors call attention to the lack of knowledge of the heats of fusion of organic substances, and utter a needful warning in pointing out that for the heats of fusion of solids there is no generalisation analogous to Trouton's rule for the molecular heats of volatilisation of liquids.

C. S.

**Heats of Combustion of Terpenes and Styrenes.** KARL AUWERS, WALTER A. ROTH, and FRITZ EISENLOHR (*Annalen*, 1910, 373, 267—290).—The molecular heats of combustion, expressed in Calories, of the following terpenes have been measured: *d*-limonene, 1466; dipentene, 1462; sylvestrene, 1464;  $\alpha$ -phellandrene, 1434; carvenene, 1424;  $\alpha$ -terpinene, 1428; *d*- $\alpha$ -pinene, 1469; *l*- $\alpha$ -pinene, 1467; camphene (liquid), 1471; sabinene, 1475.

Since empirical expressions for the determination of "calculated values" of heats of combustion are not trustworthy, the following method is adopted to obtain values whereby the thermal and the optical (refractivity and dispersivity) behaviours may be compared. The mean value, 1464, of the molecular heats of combustion of limonene, dipentene, and sylvestrene, three hydrocarbons containing two double (not conjugated) linkings, is taken as the "normal value" of the molecular heat of combustion of hydrocarbons of the terpene group. The molecular "depression," that is, the difference, expressed as a percentage, between the normal value and the actual value of the molecular heat of combustion of a terpene, is compared with the exaltation of the molecular refractivity and dispersivity, calculated from the formula  $C_{10}H_{16}^-$ . In this way, it is at once obvious that terpenes containing a conjugate linking have smaller heats of combustion (about 2%) than those which do not contain such a system, and also that the thermal "depressions" are of the same order of magnitude as, but of opposite sign to, the exaltations of the

molecular refractivity; the exaltation of the dispersivity is very much greater.

The thermochemical method will not displace the more convenient spectrochemical methods of investigating the constitutions of organic compounds, but will serve as a useful auxiliary. Auwers and Eisenlohr (this vol., ii, 365) have shown that a "disturbed conjugation" diminishes the exaltation of the molecular refractivity and dispersivity; in fact, the optical evidence does not establish with certainty the presence of a conjugate linking in  $\alpha$ -phellandrene. The thermochemical method leaves no doubt about the point, since the thermal "depression" of this terpene is practically the same as those of other terpenes containing conjugate linkings.

The theory of the identity of carvenene and  $\alpha$ -terpinene receives support from the close agreement in their heats of combustion.

The parallelism between the thermal and the optical data disappears in the case of bicyclic terpenes; the presence of a 4-ring in  $\alpha$ - and  $\beta$ -pinenes instead of a conjugate linking does not cause any appreciable deviation of the heats of combustion from the normal value, whilst it does greatly affect the optical behaviour.

The molecular heats of combustion of the following styrene hydrocarbons have been measured; styrene, 1035 (freshly distilled), 1039 (after keeping for a few hours);  $\beta$ -methylstyrene, 1190;  $\beta$ -ethylstyrene, 1346;  $\alpha$ -methylstyrene, 1193;  $\alpha\beta$ -dimethylstyrene, 1347; trimethylstyrene, 1510;  $\beta\beta$ -diethylstyrene, 1665;  $\alpha$ -phenyl- $\Delta^2$ -butene, 1353;  $\alpha$ -phenyl- $\Delta^2$ -pentene, 1510 Cal.

"Normal values" in this series are obtained as follows. The difference of the molecular heats of combustion of the two last-mentioned hydrocarbons is 157 Cal.; also, the values for styrene,  $\beta$ -methylstyrene, and  $\beta$ -ethylstyrene, all of which contain an undisturbed conjugate system, differ by 155 for the first pair and by 156 for the second pair. The mean, 156, of the three values represents the thermal value of  $\text{CH}_2$ . The heat of combustion of  $\alpha$ -phenyl- $\Delta^2$ -butene, which does not contain a conjugate linking, is taken as thermally normal; by adding or subtracting 156, or multiples thereof, the normal heats of combustion of the higher and lower homologues are calculated. The variation of the actual from the normal values is much less than in the case of the terpenes, but it is again obvious that the presence of conjugate linkings is accompanied by a diminution of the heat of combustion.

In the styrene series, the presence of conjugate linkings is more accurately and simply ascertained by spectrochemical methods, but the thermochemical method is of interest, because it serves to emphasise the remarkable parallelism between the optical and the thermal properties. For example, the depression of the heat of combustion and the exaltation of the refractivity and of the dispersivity are most pronounced in styrenes with undisturbed conjugation, such as styrene itself,  $\beta$ -methylstyrene, and  $\beta$ -ethylstyrene; a simple central disturbance of the conjugate system, as in  $\alpha$ -methylstyrene and  $\alpha\beta$ -dimethylstyrene, diminishes the thermal and the optical abnormalities to about one-half to two-thirds of the original values. Further lateral disturbance, as in trimethylstyrene, causes the thermal depression to vanish



and the exaltation of the refractivity to become very small, only the dipeireivity retaining, as is frequently the case, a marked exaltation.  
C. S.

**Diazo- and Azo-compounds. Thermochemical Investigations. I.** W. SVENTOSLAVSKY (*Ber.*, 1910, 43, 1479-1488).—The following thermochemical constants have been determined: (1) Heat of diazotisation of aniline in aqueous solution = +22.8 Cal.; obtained by mixing a solution of aniline in hydrochloric acid with a solution of sodium nitrite and subtracting from the heat of the reaction the difference between the heats of neutralisation of hydrochloric and nitrous acids. (2) Heat of solution of benzenediazonium chloride = -1.84 Cal. (3) Heat of neutralisation of the diazohydroxide with hydrochloric acid = +14.26 Cal. (4) Heat of formation of the pseudo-salt,  $C_6H_5N_2ONa$ , from the diazonium chloride and sodium hydroxide solution = +5.28 Cal. (5) Heat of formation of benzene-azo- $\beta$ -naphthol from the pseudo-salt and solid  $\beta$ -naphthol = +27.22 Cal., or  $C_6H_5N_2OH$  (liq.) +  $C_{10}H_7OH$  (solid) =  $H_2O$  +  $C_6H_5N_2C_{10}H_6OH$  (solid) + 27.22 Cal. (6) Heat of diazotising aniline in acetic acid solution = +23.28 Cal.;  $NH_2Ph(HOAc)$  (liq.) +  $HNO_2$  (soln.) =  $PhN_2OAc$  (soln.) +  $2H_2O$  + 23.28 Cal. (7) Heat of solution of aniline in acetic acid = +6.75 Cal. (8) Heat of formation of *p*-dimethylaminoazobenzene in solution from benzenediazonium acetate and dimethylaniline = +18.35 Cal., and heat of solution of *p*-dimethylaminoazobenzene in acetic acid = -3.13 Cal. (9) Heat of diazotising  $\alpha$ -naphthylamine in aqueous solution = +24.82 Cal. Heat of formation of the pseudo-salt,  $\alpha-C_{10}H_7N_2ONa$  (soln.), from the diazonium chloride and sodium hydroxide solution = +4.84 Cal. (10) Heat of formation of  $\alpha$ -naphthaleneazo- $\beta$ -naphthol (solid) from the pseudo-salt and  $\beta$ -naphthol (solid) = +29.53 Cal., of the solid hydroxy-compound from the diazohydrate and solid  $\beta$ -naphthol = +34.69 Cal., and of the solid hydroxy-compound from a solution of the diazonium chloride and an alkaline solution of  $\beta$ -naphthol = +32.82 Cal. (11) The heat of formation of nitroso- $\beta$ -naphthol from solid  $\beta$ -naphthol and nitrous acid in acetic acid solution = +28.66 Cal., or for the solid nitroso-compound = +32.47.

The heat of diazotising an amine in 50% acetic acid is somewhat greater than in glacial acetic acid, owing to the hydrolysis of the acetate of the amino in the 50% acid.  
J. J. S.

**Diazo- and Azo-compounds. Thermochemical Investigations. II.** W. SVENTOSLAVSKY (*Ber.*, 1910, 43, 1488-1495. Compare preceding abstract).—The heat produced in mixing a solution of sulphanic acid with nitrous acid = +20.40 Cal. This when corrected by adding the heat of neutralisation of the diazo-compound and subtracting the heat of neutralisation of the amine gives +25.5 Cal.

$C_6H_5\begin{smallmatrix} SO_3 \\ \diagup \\ N_2 \end{smallmatrix} + 2NaOH = SO_3Na \cdot C_6H_5 \cdot N_2ONa + H_2O + 10.7 \text{ Cal. and}$   
 $SO_3H \cdot C_6H_5 \cdot NH_2 + NaOH = H_2O + SO_3Na \cdot C_6H_5 \cdot NH_2 + 10.45 \text{ Cal., and}$   
 the difference between 10.45 and the heat of neutralisation of benzene-

sulphonie acid (13.6 Cal.) gives the value of the heat of inner salt formation of sulphanilic acid.

The reaction between sulphanilic acid and sodium nitrite solution proceeds slowly, and gives +16.20 Cal., or, since the difference between the heats of neutralisation of nitrous and sulphanilic acids is 0.2 Cal.,  $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  (soln.) +  $\text{HNO}_2$  (soln.) =  $\text{H}_2\text{O}$  +  $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OH}$  (soln.) + 16.0 Cal.

The heat of formation of the pseudo-salt,  $\text{SO}_3\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{ONa}$ , from a solution of the diazohydroxide and sodium hydroxide solution = +5.46 Cal.

The heat of formation of methyl-orange from dimethylaniline and diazobenzenesulphonic acid = 33.48 Cal.

The conclusion is drawn that the conversion of a diazonium hydroxide,  $\text{OH}\cdot\text{NR}'\text{N}$ , into a diazohydroxide,  $\text{RN}'\text{N}\cdot\text{OH}$ , is accompanied by little or no heat change.

The diazotising of anthranilic acid in aqueous solution gives rise to +21.42 Cal.

The heat of neutralisation of anthranilic acid by sodium hydroxide solution is +10.5 Cal., and that of *o*-diazobenzoic acid +6.56.

The heat of coupling *o*-diazobenzoic acid with  $\beta$ -naphthol in alkaline solution is +33.98 Cal., and as this value agrees with the heats of formation of hydroxyazobenzene (+32.85) and hydroxyazonaphthalene (+34.68), the conclusion is drawn that in alkaline solution the diazobenzoic acid contains a free  $\text{N}'\text{N}\cdot\text{OH}$  group.

J. J. S.

**Calorimetric Observations of the Reciprocal Coagulation of Ferric Hydroxide and Silver Hydrosols.** FRIEDRICH DOERINGKEL (*Zeitsch. anorg. Chem.*, 1910, 67, 161—166. Compare this vol., ii, 269).—The two colloids used for the experiments are a 5% solution of ferric hydroxide and a solution containing 9% of metallic silver and 1% of a protective colloid. The apparatus is the same as that previously used. In each experiment, 250 c.c. of each solution are employed, and the concentration of the silver colloid is expressed as the percentage of the total colloid in the united volume of 500 c.c. The heat of dilution of both colloids with water is zero. The heat of coagulation increases with the percentage of silver colloid, reaching a maximum at 60—70%, and then falling rapidly. The optimum of coagulation does not coincide with this maximum, but corresponds with 70—80% of silver colloid. Coagulation is retarded by the presence of a large excess of either substance. The colloid used to protect the silver is without action on ferric hydroxide.

Silver hydrosol is coagulated by ammonium nitrate if the concentration of the latter exceeds 40%, and the precipitate becomes perfectly soluble after washing until free from electrolyte. The heat of coagulation is +1—2 cal. per gram of silver. Aluminium sulphate, even in 1.7% solution, causes complete irreversible coagulation, the heat of solution being negative, and due almost entirely, if not entirely, to the protective colloid.

C. H. D.

**Thermal Properties of Solids and Liquids.** S. LUSSANA (*Nuovo Cim.*, 1910, [v], 19, i, 182—207).—The author has inves-

tigated the compressions of a number of metals and alloys by a modification of the method previously described (*ibid.*, 1904, [v], 7, 355), the results being briefly as follows:

With aluminium the coefficient of compressibility ( $k$ ) increases proportionally with rise of temperature, and the value of the coefficient of expansion ( $\alpha$ ) increases with rise of temperature and diminishes with increase of pressure. For bismuth, the values of  $k$  increase almost proportionally with rise of temperature, but at the higher temperatures diminish appreciably with increase of pressure;  $\alpha$  increases with rise of temperature, and diminishes with increase of pressure. With antimony,  $k$  increases almost in proportion with temperature, and  $\alpha$  increases with rise of temperature and diminishes with increase of pressure.

The compressibilities of a large number of alloys were measured, the principal results being that (1) the compressibility does not obey the law of mixtures; (2) in general, the compressibility is diminished by the initial addition of an extraneous substance; (3) the compressibility increases with rise of temperature, and the coefficient of expansion diminishes with increase of pressure.

T. H. P.

**Attraction Pressure.** ISIDOR TRAUBE (*J. Physical Chem.*, 1910, 14, 452—470).—A résumé of the author's communications on cohesion pressure (compare Abstr., 1908, ii, 565; 1909, ii, 216, 325, and 647).

T. S. P.

**Theory of Attraction Pressure.** ISIDOR TRAUBE (*J. Physical Chem.*, 1910, 14, 471—475).—A theoretical paper of a qualitative nature with respect to the hydrating effect of cohesion pressure. It is assumed that the molecules and ions of a solute surround themselves, similarly to the condensation nuclei of gases, with an envelope of water molecules, the intensity of attraction between the molecules (or ions) and the water envelope corresponding with the cohesion pressure. Various deductions are made which are not in accordance with the dissociation theory of Arrhenius, and the osmotic pressure theory of van't Hoff.

T. S. P.

**Viscosity-coefficients of Vapours and their Variation with Temperature.** KARL RAPPENNECKER (*Zeitsch. physikal. Chem.*, 1910, 72, 695—722).—The viscosities of a number of vapours have been measured at 100° and 212° by a modification of a method described by Pedersen (*Physical Review*, 1907, 25, 230). The values of  $\eta \times 10^{-4}$  at 100° (where  $\eta$  is the absolute viscosity coefficient) are as follows: isopentane 885.1, ethyl ether 967.1, acetone 942.7, ethyl alcohol 1600, methyl acetate 1015, ethyl acetate 954.6, chloroform 1307, benzene 930.2. From the values at 100° and 212°, the variation of the viscosity with temperature is expressed as proportional to the  $n^{\text{th}}$  power of the absolute temperature, and with the exception of chloroform and ether, which probably act on the mercury in the apparatus, the value of  $n$  is about 1.1.

The temperature-coefficients thus found are in satisfactory agreement with the formula of Sutherland,  $T^{0.5}/(1 + C/T)$ , where  $C$  is proportional

to the work gained when two molecules are brought into contact from a great distance, and with a somewhat similar formula obtained by Reinganum.

From the results, by means of a formula proposed by Reinganum (Abstr., 1909, ii, 223), the molecular volumes and the absolute number of molecules in a gram-molecule of vapour are calculated. The values for the molecular volumes are in excellent agreement with those determined directly by Kopp. For the absolute number of molecules in a gram-mol., the value  $6.26 \times 10^{23}$  is obtained; it is independent of the nature of the substance, as the molecular-kinetic theory requires and agrees almost exactly with that calculated from quite different premises by Planck and by Rutherford and Geiger. G. S.

**Viscosity of Certain Metals and its Variation with the Temperature.** CHARLES E. GUYE and SAUL MINTZ (*Arch. sci. phys. nat.*, 1910, [iv], 29, 474—475).—An amplification of the details given in a previous paper (Abstr., 1908, ii, 930). Some corrections are also made. T. S. P.

**The Influence of the Reaction of the Medium on Adsorption.** LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1910, 25, 359—366).—The adsorbents employed were carbon, kaolin, and ferrous hydroxide. With certain substances, it was found that the maximum of adsorption took place with a certain definite hydrogen ion concentration (albumin); in others, a minimum of adsorption took place with definite hydrogen ion concentration (amylase), whereas with a third class of substances (trypsin) a continuous change in the amount of adsorption occurred on altering the reaction of the medium, without the attainment at any time of a definite maximum or minimum. S. B. S.

**Adsorption and Colloid Precipitation.** HUGO MORAWITZ (*Koll. chem. Beihefte*, 1910, 1, 301—330).—With the object of testing Freundlich's theory relative to the connexion between adsorption and colloidal precipitation, measurements have been made of the adsorption of electrolytes by animal charcoal, and also of the influence of these on the precipitation of colloidal gold solutions.

From adsorption experiments with aqueous solutions of zinc, lead, copper, silver, and mercuric salts, it is found that the magnitude of the adsorption is dependent on the nature of the cation and the anion, and on the degree of ionisation. In general, the adsorption increases as the electro-positive character of the cation diminishes. Mercuric chloride is adsorbed in exceptionally large quantities, the adsorption of the substance being thirty times as great as that of zinc chloride.

In general, the results of the coagulation experiments indicate that those salts which are most readily adsorbed by animal charcoal are the most active in bringing about the precipitation of colloidal gold. Differences in the two series of experimental data indicate, however, that the phenomena are complicated by factors which mask to a considerable extent the influence of the specific chemical nature of the electrolyte. In the case of certain salts of the heavy metals, the

coagulative capacity towards a slightly acid colloidal gold solution is very much smaller than towards a feebly alkaline solution. The ratio of the two influences in the case of mercuric chloride is of the order of a thousand.

H. M. D.

**Relationships between Adsorption and Toxicity.** WOLFGANG OSTWALD and A. DERNOSCHECK (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 297. Compare Abstr., 1906, ii, 112; 1907, ii, 981).—In a previous paper it was shown that the relationship between the concentration and the toxicity of sea-water solutions towards *Gammarus* could be approximately represented by an exponential (adsorption) formula. The necessity of taking into account the quantity of salt which is normally present in the tissue is now pointed out, and the single toxicity formula is replaced by two, one of which holds for salt solutions more concentrated than the "normal," and the other for solutions of smaller concentration.

By reference to the previous data for *Gammarus*, and new results obtained with *Daphnia magna*, it is shown that the modified toxicity formulæ are capable of representing the experimental observations more accurately than the simple exponential formula.

An explanation of the influence exerted by salts on one another when present in the same toxic solution is given on the basis of the adsorption theory.

H. M. D.

**The Internal Friction of Albumin Solutions.** LEONOR MICHAELIS and B. MOSTYNSKI (*Biochem. Zeitsch.*, 1910, 25, 401—416).—Horse-serum was dialysed, and after varying periods of dialysis the internal friction was measured after the addition of varying quantities of acid and alkali. If the dialysis had lasted for a sufficient length of time, a fairly sharp minimum was attained, corresponding with a hydrogen ion concentration of the order  $10^{-5}$ . This is the isoelectric point. If the dialysis had not been of sufficient duration, this minimum was less sharply defined, and a second ill-defined minimum was attained by addition of sodium hydroxide. This latter phenomena was due to an incomplete separation of the globulin.

S. B. S.

**The Inversion Points for a Fluid passing through a Porous Plug and their Use in Testing Proposed Equations of State. II. An Examination of Experimental Data.** ALFRED W. PORTER (*Phil. Mag.*, 1910, [vi], 10, 888—897).—The inversion points of nitrogen are calculated by a graphical method from Amagat's data, and shown to agree well with Dieterici's equation of state, but not with van der Waals'. For carbon dioxide (Amagat's values), the agreement with Dieterici's equation is again good, but the values lie on the lower, whereas for nitrogen they lie on the upper, portion of the theoretical curve. This is regarded as confirming the author's view that two inversion points exist for each pressure. For isopentane, ethylene, and ethyl ether, the inversion curves are very similar to that of carbon dioxide.

F. S.

**Crystals which are Absolutely Stable only under High Pressures.** ANTON SKRABAL (*Zeitsch. physikal. Chem.*, 1910, 73, 171—172).—Tammann (compare Abstr., 1909, ii, 983) has pointed

out that Ostwald's rule, according to which the order of separation of forms of different degrees of stability is determined by the smallest diminution of free energy, is not valid, but the author shows that a modification of this rule proposed by him (compare *Zeitsch. Elektrochem.*, 1908, 14, 529), according to which there is a connexion between the velocity of a change and the stability of the reaction products in such a way that the more rapid the reaction the greater is the possibility of obtaining the less stable products, is in accordance with the experimental facts.

G. S.

**Gelatinisation of Silicic Acid.** I. NICOLA PAPPADÀ and C. SADOWSKI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 292—297).—The influence of electrolytes on the gelatinisation of solutions of silicic acid and the relationship between the processes of gelatinisation and coagulation (flocculation) have been examined. Whether gelatinisation or coagulation takes place depends on the concentration of the colloidal solution, the former occurring with concentrated and the latter with more dilute solutions. The influence of different electrolytes on the velocity of the two processes is very nearly the same. From experiments with the alkali metal chlorides, it is found that the velocity increases with the atomic weight of the cation. Comparative observations with the alkaline-earth metal chlorides show that the velocity increases with the magnitude of the electric charge on the cations.

A theory is advanced in explanation of the observations, and according to this the gelatinisation effect of different ions is determined by their rates of diffusion.

H. M. D.

**Distribution of Iodine between Certain Organic Solvents.** M. LANDAU (*Zeitsch. physikal. Chem.*, 1910, 73, 200—211; *J. Russ. Phys. Chem. Soc.*, 1910, 42, 377—395. Compare Waentig, this vol., ii, 117).—The distribution of iodine between glycerol and benzene and between glycerol and carbon tetrachloride has been determined at 25°, 40°, and 50°. The ratio of the concentration in benzene and in carbon tetrachloride to that in glycerol increases regularly with the iodine concentration, in agreement with the views of Beckmann and of Hantzsch and Vogt, that in solvents forming brown solutions (such as glycerol) iodine is partially combined with the solvent, whilst in violet solutions it is uncombined.

Further, the distribution of iodine between ethyl ether and ethylene glycol, both of which give brown solutions, was measured at 0° and 25°, and it was found that the distribution ratio is practically independent of the dilution. The direct determination of the distribution of iodine between two violet solutions is not possible, as all such solvents are partially or completely miscible, but the distribution between benzene and carbon tetrachloride has been calculated from the results of each with glycerol. In this case, also, the ratio is practically independent of the concentration, and the same is true for chloroform and carbon tetrachloride, also calculated indirectly. There is evidence also of partial combination in violet solutions, although to a much smaller extent than in the brown solutions.

The amount of combination in some solvents at low temperatures has been calculated on the assumption, which is only approximately true, that at high temperatures and in concentrated solutions the proportion of iodine combined is negligible. From a formula deduced on this basis, it is calculated that the proportion of iodine combined with glycerol at 25° varies from 46% to 7.6% as the concentration is increased from 0.0016 to 0.0208 mol. per litre.

G. S.

**The System Phenylhydrazine-Water.** JAN J. BLANKSMA (*Chem. Weekblad*, 1910, 7, 417-425).—The melting points, boiling points, and specific gravities of various mixtures of phenylhydrazine and water have been determined.

When the results are plotted with temperatures as ordinates and percentages as abscissa, a curve is obtained indicating that with water phenylhydrazine only forms one hydrate. On addition of water to phenylhydrazine, the m. p. falls to the eutectic point (16.6°) of phenylhydrazine + hydrate, phenylhydrazine separating out. On addition of more water, the hydrate  $C_6H_5NH \cdot NH_2 \cdot \frac{1}{2}H_2O$  separates, the m. p. first rising to 26.2°, that of the hydrate, and then falling to 20.4°, when separation into two layers takes place. Between the limits 60.1° and 11.6° of phenylhydrazine, the m. p. remains constant at 19.8°. On addition of more water, the liquid becomes homogeneous, and the hydrate separates out until the eutectic point (hydrate + water) is reached at -0.7°. Ice then separates from this temperature to 0°. The shape of the melting-point curve of the hydrate indicates that it is gradually dissociated in the fused liquid.

A mixture of 30% of phenylhydrazine and 70% of water, which has been made homogeneous by warming, becomes opalescent on cooling to 57°. The opalescence increases as the temperature falls, and at 35° the liquid becomes suddenly opaque and separates into two layers. All mixtures with compositions approximating to that of the critical mixture exhibit these opalescence phenomena.

When a mixture of about 33% of phenylhydrazine and 67% of water is made homogeneous by warming to 60-65°, agitation produces considerable foaming. This foaming vanishes at 55°, its disappearance coinciding with the appearance of two layers. On cooling to 45°, the heterogeneous liquid regains its property of foaming, and retains it to about 10°, when the hydrate crystallises out, yielding a thick deposit full of air bubbles. All mixtures containing 40% to 15% of phenylhydrazine exhibit this phenomenon. Mixtures with about 10.9% and also 40-60% of phenylhydrazine do not foam in the heterogeneous region.

For mixtures of phenylhydrazine and water, the liquid and vapour curves do not approach at the concentration of the hydrate, indicating complete dissociation of the hydrate in the state of vapour. The curves also indicate that the principal product of the initial part of the distillation is water, the h. p. of the residual liquid only rising slightly. When most of the water has passed over, the h. p. rises rapidly to that of phenylhydrazine.

The densities of mixtures of phenylhydrazine and water give no indication of the formation of a hydrate.

A. J. W.

**Influence of the Solvent on the Equilibrium Constant.** LEO PISSARJEWSKY and I. BELENOWSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 530—536. Compare Pissarjewsky and Trachoniotowsky, this vol., ii, 402).—The authors have measured the constant  $K = C_{\text{Ag}(\text{CN})_2} / C_{\text{Cl}}$  of the reaction  $2\text{AgCN} + \text{KCl} = \text{KAg}(\text{CN})_2 + \text{AgCl}$  at 25° in water, 10·5% aqueous mannitol, and 23·7% aqueous glycerol, the results, together with the values of  $\eta$  for the different solvents, being as follows:

	$K$ .	$\eta$ .
Water .....	0·030	1·00
10% mannitol solution .....	0·027	1·36
23·7% glycerol " .....	0·029	1·95

The value of  $K$  is hence practically independent of the solvent, in spite of the considerable variation of the viscosity (compare Lucas, *Abstr.*, 1904, ii, 715).

Similar measurements were made of  $K = C_{\text{Ag}(\text{CN})_2} / C_{\text{Br}}$  for the reaction:  $2\text{AgCN} + \text{KBr} = \text{KAg}(\text{CN})_2 + \text{AgBr}$  at 25° in aqueous solutions of various alcohols, the results being as follows:

	$K$ .	$\eta$ .
30% glycol solution .....	3·8	2·02
20% erythritol solution .....	5·9	1·61
50% methyl alcohol solution ...	7·15	1·62

Here, again, no relation exists between  $K$  and  $\eta$ .

T. H. P.

**Influence of Insoluble Salts in Equilibria.** LEO PISSARJEWSKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 536—537).—According to Laschtschenko (*Trans. Phys. Chem. Soc. Kharkoff Univ.*, 1908, 35, part 21), the course of a reversible heterogeneous reaction in a solvent is influenced distinctly by the degree of solubility of sparingly soluble salts and by a change of this solubility in relation to changes in composition and concentration of the liquid phase of the system. The author's results (*Abstr.*, 1909, ii, 866; this vol., ii, 402, and preceding abstract) give no indication of any such influence.

T. H. P.

**Free Energy of Chemical Action in Mixtures of Water with Non-electrolytes.** III. LEO PISSARJEWSKY and K. ZEMBISKY (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 537—544).—The authors have measured the constant  $K = C_{\text{Ag}(\text{CN})_2} / C_{\text{Br}}$  of the reaction  $2\text{AgCN} + \text{KBr} = \text{KAg}(\text{CN})_2 + \text{AgBr}$  at 25° in water, for which Lucas (*Abstr.*, 1904, ii, 715) found the value 7·1, and in aqueous solutions of various non-electrolytes, and have calculated the corresponding values of the free energy of the reaction by means of the equation:  $A = RT \log K$ . The numbers obtained, which, together with those of  $\eta$ , are given in the following table, show that no relationship of a general character exists between the value of  $\eta$  for any solvent and the values of  $K$  and  $A$  for a reaction taking place in that solvent.

	$K$ .	$A$ .	$\eta$ .
Water .....	8·1	1270 cal.	1·0
10·5% mannitol solution .....	6·6	1121 "	1·36
9·8% glycerol solution .....	6·5	1110 "	1·3
23·7% glycerol solution .....	9·3	1322 "	1·95
49·9% glycerol solution .....	11·5	1450 "	5·5
50·0% acetone solution .....	6·9	1146 "	1·25
75·0% methyl alcohol solution..	21·0	1798 "	0·86



The empirical formula,  $A = A_0^1 - 100B\eta$ , deduced by Pissarjewsky and Levites (Abstr., 1908, ii, 570), is found to be inapplicable in this instance. There exist, however, indications of an empirical relation between  $A$  and  $\eta$  for a particular group of solvents, such as aqueous solutions of glycerol, probably owing to the formation of a definite compound between the solvent and the solute. The fact that the reaction proceeds in either direction more slowly in 50% acetone or 74% methyl alcohol than in 50% glycerol is also a probable indication of the formation of compounds between the ions of the dissolved compounds and the molecules of the solvent. T. H. P.

**Equilibria in Ternary and Quaternary Systems in which Two Liquid Layers Occur.** F. FONTEIN (*Zeitsch. physikal. Chem.*, 1910, 73, 212—251).—The data required for the construction of the complete equilibrium diagram for the system amyl alcohol-ethyl alcohol-water-sodium chloride have been determined, and some measurements have also been made with methyl instead of ethyl alcohol.

The equilibrium between the liquid phases in the system amyl alcohol-ethyl alcohol-water has been determined by solubility measurements according to Alexéeff's method, and from the results, the binodal curves for 0°, 15.5°, and 28° are constructed in the usual way. It can be deduced from the graphic representation that when ethyl alcohol is slowly added to a saturated aqueous solution of amyl alcohol at 0°, a separation into two layers at first occurs, but later the mixture becomes homogeneous; at 15.5° and 28° no separation occurs. These conclusions have been confirmed by experiment.

The position of conjugate points on the diagram has been determined by the separate analysis of two layers in equilibrium. The special methods used are fully described. The critical solution at 15.5° contains 20% of amyl alcohol, 27% of ethyl alcohol, and 53% of water; at 28° it contains 20% of amyl alcohol, 25% of ethyl alcohol, and 55% of water. The composition of the critical solution can also be derived from the distribution coefficients of the components.

Similar experiments have been made with methyl alcohol instead of ethyl alcohol, and the corresponding binodal lines for the two systems are compared.

As regards the equilibrium water-amyl alcohol-sodium chloride, a number of conjugate layers were prepared at 28° and analysed. In the upper layer, which consists of a saturated solution of water in amyl alcohol, very little sodium chloride dissolves.

A number of solubility determinations were also made at 28° with the four components in order to fix some further points of the complete equilibrium diagram. The results are also given in tabular form.

G. S.

**Rate of Decomposition of Barium Ethyl Sulphate in Acid and Alkaline Solutions at Different Temperatures.** ROBERT KREMANN (*Monatsh.*, 1910, 31, 165—176).—The reaction between barium ethyl sulphate and water may be represented by the equation:

$\text{Ba}(\text{SO}_4\text{Et})_2 + 2\text{H}_2\text{O} = \text{BaSO}_4 + \text{H}_2\text{SO}_4 + 2\text{EtOH}$  (1), but the sulphuric acid thus formed reacts with more of the barium salt,  $\text{H}_2\text{SO}_4 + \text{Ba}(\text{SO}_4\text{Et})_2 = \text{BaSO}_4 + 2\text{HEtSO}_4$  (2), so that the total reaction is  $2\text{Ba}(\text{SO}_4\text{Et})_2 + 2\text{H}_2\text{O} = 2\text{BaSO}_4 + 2\text{EtOH} + 2\text{HEtSO}_4$  (3). But in addition to this, the ethyl hydrogen sulphate is slowly decomposed by the water, yielding ethyl alcohol and sulphuric acid, the latter then reacting with the barium salt,  $\text{HEtSO}_4 + \text{H}_2\text{O} + \text{Ba}(\text{SO}_4\text{Et})_2 = \text{BaSO}_4 + \text{EtOH} + 2\text{HEtSO}_4$  (4).

The rate of decomposition of the barium salt with pure water and with 0.5*N*- and *N*-solutions of hydrochloric acid has been determined at 55° and 66° by weighing the amount of barium sulphate formed after given intervals of time. The curves show that with *N*-hydrochloric acid the decomposition is more rapid than with water, but that with 0.5*N*-acid the rate of decomposition is considerably slower than when water alone is used. This may be due to the fact that the reaction represented by equation (3) is retarded by the presence of hydriions, whereas the reaction (4) is accelerated by hydriions. With very dilute acid, the retarding action is the more pronounced, but with more concentrated acid the accelerating action becomes so. This is supported by the fact that in aqueous solutions the decomposition is less the more concentrated the solution.

Similar experiments have been made with standard solutions of sodium hydroxide. The sodium ethyl sulphate formed is stable, and is not hydrolysed to any appreciable extent by the alkali. The decomposition proceeds more slowly than in neutral solution, and the rate increases roughly proportionally to the concentration of the alkali. At the beginning, the reaction is practically unimolecular, but the value of *K* diminishes as the alkali is used up. J. J. S.

**Kinetics of the Decomposition of Quaternary Ammonium Salts in Chloroform Solution.** EDGAR WEDEKIND and F. PASCHKE (*Zeitsch. physikal. Chem.*, 1910, 73, 118—128. Compare Abstr., 1908, i, 334).—The rate at which certain quaternary ammonium salts of the type  $\text{NR}_4\text{X}$ , where X represents a halogen atom, decompose in chloroform solution according to the equation  $\text{NR}_4\text{X} = \text{NR}_3 + \text{RX}$  is represented in the first instance by an equation of the first order, but the "constants" increase somewhat during the reaction, and are the greater the smaller the initial concentration. This is now shown to be due to partial polymerisation to double molecules in chloroform solution; only the simple molecules undergo decomposition.

The experiments were made with propyl- and allyl-phenylbenzyl-methylammonium bromides. The degree of polymerisation in different dilutions was determined from the results of distribution measurements between water and chloroform at 25° in the usual way, a correction being applied on account of the fact that the salts are partly ionised in aqueous solution. In connexion with the last-mentioned point, the molecular conductivities of the salts were determined in water (and also in absolute alcohol) at 25°.

The rate of decomposition of *d*-phenylbenzylmethylpropylammonium iodide is diminished by addition of the corresponding nitrate. G. S.

**Catalysis in Heterogeneous Systems.** The Equilibrium  $Ti^{III} + H \rightleftharpoons Ti^{IV} + H$ , and the Reaction  $HCN + 2H_2 = CH_3 \cdot NH_2$ . HENRY G. DENHAM (*Zeitsch. physikal. Chem.*, 1910, 72, 641—694).—It has been shown by Diethelm and Foerster (compare Abstr., 1908, ii, 360) that in sulphuric acid solution there is an equilibrium between trivalent and quadrivalent titanium, represented by the equation  $Ti^{III} + H \rightleftharpoons Ti^{IV} + H$ , and that in the presence of platinised platinum the equilibrium can be reached from both sides. The position of the equilibrium under varying conditions and the kinetics of the two reactions have now been investigated by the author. As catalyst, platinised platinum net in the form of a cylindrical stirrer, driven at constant speed, was used. Except when otherwise mentioned, the solutions contained excess of sulphuric acid; in the majority of cases the acid was normal.

The position of the equilibrium depends on the pressure of the hydrogen. At 638 mm. pressure and 25°, the equilibrium mixture contains about 38.7% of quadrivalent titanium; at 416 mm., 43.5%, and at 209 mm., 61.1%. Rise of temperature also favours the production of  $Ti^{IV}$ ; at 35° the equilibrium mixture contains 42%, and at 45° 49% of quadrivalent titanium.

The reversible reactions,  $Ti^{III} + H \rightleftharpoons Ti^{IV} + H$ , were followed by measuring the rate of the appearance and disappearance of hydrogen respectively, and, apart from some initial disturbances, are both unimolecular. Variation of the hydrogen pressure between 10 and 76 cm. had practically no effect on the reaction velocity. The temperature-coefficient of the reaction-velocity is only 1.29 for an increase of 10°, and for this and other reasons, the conclusion is drawn that the speed of the reaction is determined by the rate at which the reacting substances diffuse to the platinum surface.

When the position of the equilibrium is determined from the amount of hydrogen absorbed instead of by the more trustworthy method of titration with permanganate, different results are obtained, and it is suggested that the excess of hydrogen taken up is due to the presence of higher compounds in which the titanium is quinquevalent or sexavalent.

The rate of the reaction when titanium chloride and hydrochloric acid is used is very nearly the same as with the sulphate, but the position of equilibrium in the two cases is different. In *N*/1-hydrochloric acid the equilibrium mixture contains 53%, in 2*N*-acid about 26.6%, of quadrivalent titanium.

Hydrocyanic acid does not retard the action of platinum in this case, but in acid solution under the conditions of the experiment is completely reduced to methylamine.

In connexion with the conclusion that the speed of the reaction is determined by a diffusion process, the general question of reaction velocities in such heterogeneous systems is discussed, and it is suggested that the high concentration of the reacting substances on the surface of the platinum, due to adsorption, is of considerable importance in this connexion (compare Nernst and Brunner, Abstr., 1904, ii, 315; Sand, Abstr., 1905, ii, 233; Senter, *ibid.*, ii, 377, 379;

Teletoff, Abstr., 1906, ii, 95; Bayliss, Abstr., 1906, ii, 344; Lewis, Abstr., 1909, ii, 383). G. S.

**Specific Stereochemical Behaviour of Catalysts.** KASIMIR FAJANS (*Zeitsch. physikal. Chem.*, 1910, 73, 25—96).—Part of the work described in the paper has already been published (compare Abstr., 1908, ii, 268). The rate of elimination of carbon dioxide from the optically active camphorcarboxylic acids has also been studied in acetophenone solution in the presence of a number of alkaloids. With quinine, the *l*-acid decomposes 46% faster than the *d*-acid, and with quinidine, the *d*-acid decomposes 46% faster than the *l*-acid. The differences between the rates of decomposition of the two acids in the presence of other alkaloids are less pronounced.

The fact that the rate of reaction of the free acids is much less than when bases are added is ascribed to salt formation, the salts being decomposed much more readily than the free acids. There is evidence, however, that in some cases salt formation is not complete, but an equilibrium exists, represented by the equation:  $C_{\text{base}}C_{\text{acid}}/C_{\text{salt}} = K$ , and some of the deviations from a simple unimolecular reaction are thus accounted for. The temperature-coefficient for  $10^\circ$  for the reaction between  $80^\circ$  and  $90^\circ$  is about 3.1 in water, benzene, and acetophenone. The velocity of decomposition of the inactive acid in the absence of a base is about 3% less than that of the active acids, indicating the presence of a small proportion of the racemic acid.

A few preliminary experiments with bromocamphorcarboxylic acids show that the rate of decomposition in the presence of an equivalent amount of quinine or quinidine is about two thousand times greater than that of the free acids under equivalent conditions.

The optical activation of inactive camphorcarboxylic acid has been brought about by heating with quinine until partial decomposition has occurred, and then interrupting the action. As anticipated, the unchanged acid was slightly dextrorotatory, the camphor formed slightly levorotatory. Corresponding results were obtained with quinidine.

Bodenstein (*Zeitsch. Elektrochem.*, 1909, 15, 394) has pointed out that the acceleration of the decomposition of an acid by addition of a base, resulting in salt formation, can scarcely be regarded as an example of catalysis, but the author points out that it is in accordance with Ostwald's definition of a catalytic action, the base in this case remaining unaltered at the end of the experiment.

The theoretical bearings of the results, more particularly with reference to asymmetric syntheses by catalysis, and to analogies with the specific action of enzymes, are discussed in great detail, with numerous references to the literature of the subject. The specific behaviour of the enzymes to optical isomerides is only quantitative in character, as the capacity to combine with an enzyme is not confined exclusively to one of the optical antipodes. Suggestions are made to account for the peculiarities in the synthetic action of enzymes on the sugars. G. S.

**Atomic Weight Accurately a Function of the Volution of Ideal Space-Symmetry Ratios.** NEWMAN HOWARD (*Chem. News*, 1910, 101, 265).—A restatement of views expressed previously in reference to the connexion between atomic weight values and certain geometric ratios (compare this vol., ii, 490).  
H. M. D.

**The Periodic System.** A. VOSMAER (*Chem. Weekblad*, 1910, 7, 483—484).—A criticism of the periodic table, pointing out that it does not indicate any relation between atomic weights and electrical conductivity, melting point, hardness, or changing valency.

A. J. W.

**Radius of the Sphere of Action of a Molecule.** R. D. KLEEMAN (*Phil. Mag.*, 1910, [vi], 19, 840—846).—The radius of the sphere of action of a molecule is deduced by means of theoretical expressions from the surface-tension of the liquid and the latent heat of evaporation and their change with temperature. Values of the former are obtained from the work of Ramsay and Shields, and of the latter from that of Mills. The results for a number of carbon compounds indicate that the diameter of the sphere of action is very nearly of the same magnitude as the distance of separation of the molecules in a liquid. It is further deduced that the factor expressing the variation of the diameter of the sphere of action with temperature must have the same value for all liquids at corresponding states, and that the values of  $\lambda/\rho L$  ( $\lambda$  is the surface-tension,  $\rho$  the density, and  $L$  the latent heat of evaporation) for all liquids at corresponding temperatures should be constant, and are approximately so.  
F. S.

**Experimental Illustration of the Law of Multiple Proportions.** JOSEPH H. KASTLE (*Amer. Chem. J.*, 1910, 43, 553—556).—The following is recommended as a lecture experiment to demonstrate the law of multiple proportions. Finely-powdered cuprous chloride (0.1—0.25 gram) is weighed in a porcelain boat, which is afterwards placed in a combustion tube and heated in a gentle current of chlorine until the weight is constant. The boat is allowed to cool to a certain extent in the stream of chlorine, and is then transferred to a weighing bottle, which is allowed to cool in a desiccator and is afterwards weighed. The anhydrous cupric chloride is dissolved in water, and the copper estimated either by electrolysis or by precipitation with zinc. It is found that the conversion of the cuprous chloride into the cupric salt and the weighing of the cupric chloride can be completed and the estimation of the copper begun in one hour. The estimation can be finished and the copper weighed at the next lecture. E. G.

**Clearing of Emulsions.** RICHARD FANTO and MILAN J. STRITAR (*J. pr. Chem.*, 1910, [ii], 81, 564—568).—In this preliminary paper the authors describe a method whereby emulsions can be electrically cleared. With a continuous current (at 220 volts and a lamp resistance) the two wires, touching below the surface of the emulsion, are moved about in the liquid, which is thereby cleared. When a spark discharge is employed, one terminal of the induction coil is connected

to a wire round the neck of a separating-funnel, the edge of which is moistened with water or other conductor; the other terminal is connected with the loop of a wire passing through the cork closing the funnel and dipping into the emulsion contained therein. C. S.

**Ultra-filtration.** F. J. J. BUYTENDYK (*Chem. Weekblad*, 1910, 7, 425—431).—An account of previous work on filtration under pressure through porous clay saturated with gelatin or silicic acid. The author finds that a freshly-prepared solution of hæmoglobin is kept back by a 4% gelatin filter, but not after some days. Another filter retained hæmoglobin in serum, but allowed hæmoglobin from the alimentary canal of the leech to pass. A 5% gelatin filter retained hæmoglobin, but not the alkaline hæmatin derived from it. Serum-globulin containing 0.75% of sodium chloride is kept back by a 5% filter, the ultra-filtrate containing 0.67% of the chloride. When this globulin solution was diluted so as to contain 0.25% of salt, the ultra-filtrate contained 0.24%. At a dilution of 0.125% the ultra-filtrate contained the same proportion (0.125%). A. J. W.

**Automatic Washing Apparatus.** Ach. GRÉGOIRE (*Bull. Soc. chim. Belg.*, 1910, 24, 223—224).—The apparatus consists of three parts, namely, a large Mariotte's bottle containing the wash-water, a funnel containing the substance to be washed, and a second funnel situated below the first and containing a siphon fitted into the neck. The shorter limb of another siphon tube reaches to the bottom of the Mariotte bottle, the longer limb ending a few millimetres above the opening of the siphon in the lower funnel. The side tubulure of the Mariotte bottle is fitted with a tube which opens on to the first funnel.

The action is as follows: wash-water runs on to the first funnel from the side-tube of the bottle. The filtrate runs into the lower funnel, and, as soon as it rises to the level of the siphon tube from the Mariotte bottle, air is prevented from entering the latter, and the flow of wash-water is stopped. The filtrate finally rises above the level of the siphon in the lower funnel, which immediately empties itself, thus again admitting air to the Mariotte bottle and allowing more wash-water to flow into the first funnel, and so on. T. S. P.

**Improved Siphon.** C. A. JACOBSON and S. C. DINSMORE (*J. Amer. Chem. Soc.*, 1910, 32, 810—811).—A siphon is described, consisting of a pipette bearing a side-arm from the bulb, which is bent parallel to the pipette and dips into the flask containing the liquid to be siphoned. A rubber bulb is attached to the upper end of the pipette, and a piece of rubber tubing carrying a spring clip is fitted to the lower end. The rubber bulb is compressed, and the clip is closed. On gently diminishing the pressure on the bulb, liquid is drawn into the pipette, so that on releasing the clip the siphon will act. The apparatus is simple and easy to manipulate, is specially adapted to cases of extraction with non-miscible solvents, and is also useful for decanting the supernatant liquid from precipitates. It is very convenient for the filtration of colloidal solutions, and, in such cases, the flow through

the siphon is regulated by means of a chip of wood to hold the spring-clip open so that the rate of flow through the siphon is equal to that through the filter.

E. G.

**Apparatus for Drying Flasks, etc.** CHARLES BASKERVILLE and RESTON STEVENSON (*J. Amer. Chem. Soc.*, 1910, 32, 650—651).—Dry air entering a vertical tube near the bottom is heated by a red-hot platinum wire wound round an inner porcelain tube at the top of the apparatus. The hot air which streams out from small apertures at the top dries the flasks, beakers, test-tubes, etc., placed over the tube. Electricity is the source of heat employed. The platinum wire in the coil is of three different diameters, the thinnest at the lowest part and the thickest at the top of the coil; by this arrangement the coil glows with nearly uniform brightness throughout its length.

L. DE K.

**An Automatic Toepler Pump Designed to Collect the Gas from the Apparatus being Exhausted.** BERTHAM D. STEELE (*Phil. Mag.*, 1910, [vi], 19, 863—868).—A modified form of Toepler pump which can be automatically worked by a water pump for a long period, and enables samples of the extracted gas to be obtained when desired, whilst if needful, the whole of such gas can be collected for examination.

F. S.

**Preparation of Illuminating Gas as a Lecture Experiment.** NICOLAS TECLU (*Chem. Zeit.*, 1910, 34, 523).—The upper end of a Landsiedl spiral glass condenser (*B*) is fitted with a cork carrying a glass tube (*C*) holding a fish-tail burner. The lower end of the condenser is prolonged by fusing to it a T-piece having a short side-arm. To the latter is attached a hard glass test-tube (*A*) packed with small pieces of coal or wood. The remaining free end of the T-piece is fitted with a cork carrying a test-tube (*D*). On heating *A*, coal gas, water vapour, and tar are produced. The tar condenses in *D*. The water vapour is condensed in *B*, and also falls into *D*, whilst gas issues through *C* and may be burnt.

T. A. H.

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## Inorganic Chemistry.

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**Solidification of Fused Sulphur.** ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1910, 72, 752—759).—The author (compare Abstr., 1908, ii, 677—800) and others have assumed that when a homogeneous fluid mixture of  $S_2$  and  $S_8$  is allowed to cool,  $S_8$  (crystalline sulphur) at first separates pure from the liquid, whilst Krüy (Abstr., 1909, ii, 802) has suggested that mixed crystals are formed. The author now shows by microscopic observations of very thin layers of solidified sulphur that his former assumption is justified. The paper is illustrated by microphotographs.

G. S.

**Elastic Sulphur Resembling India Rubber.** P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 474—476. Compare this vol., ii, 496).—When sulphur at above  $400^{\circ}$  is poured in a thin stream into liquid air, it is obtained in the form of a thin thread of diameter 0.5—1 mm. When removed from the liquid air, this thread is quite hard and brittle, but, when the temperature rises somewhat, it assumes extraordinary elasticity. This sulphur has a polished surface, and appears pale gray in reflected light and pale yellow in transmitted light, being completely transparent and without sign of opalescence. The maximum extension of a thread about 1 mm. in diameter is approximately 5.5 times the original length, and if the extension is less than the maximum, the thread is able to return almost to its original length. The elasticity is lost in about half an hour after the thread is removed from the liquid air, the sulphur then becoming plastic and remaining so for about twenty-four hours.

T. H. P.

**Electrolytic Oxidation of Sulphurous Acid in Aqueous Solution.** ARTHUR FISCHER and G. DELMARCEL (*Bull. Soc. chim. Belg.*, 1910, 24, 236—237).—A divided cell was used, the cathode, a nickel cylinder, or else a platinum spiral being contained in a porous cell. The anode was a cylinder of platinum gauze, and surrounded the porous cell; the area was 140—150 sq. cm. The catholyte was a solution either of sulphuric acid or of sodium sulphite, the anolyte being an aqueous solution of sulphur dioxide, varying in concentration from 1 to 5%. In most cases the strength of current was 1 ampere.

Catalysts, such as copper acetate, do not increase the yield of sulphuric acid, since the platinum of the electrode acts as the catalytic agent. Better results are obtained with low than with high concentrations of the electrolyte. When oxygen begins to be liberated at the anode, there is a sudden drop in the current strength.

T. S. P.

**Degree of Ionisation of Sulphuric Acid in Mixtures of Alcohol and Water.** ROBERT KREMANN and WALTER BRASSERT (*Monatsh.*, 1910, 31, 195—200).—The degree of ionisation of sulphuric acid in various mixtures of alcohol and water has been determined by the electrical conductivity method.

As a rule, the ionisation increases with rise in temperature, except, in the case of very dilute solutions and of solutions containing much water, when it diminishes with rise of temperature. The latter may be due to experimental errors, and in no case is the effect of temperature marked.

Three curves are given showing the relationship between the degree of ionisation at  $0^{\circ}$  and the concentration of the acid for the three mixtures containing 0.8%, 6.2%, and 15.4% of water.

With dilute solutions up to 0.5 mol. per litre, the alteration of the ionisation with the water contents is quite normal, for example, shows a gradual increase as the amount of water increases. With more concentrated solutions (0.5—1.4 mols. per litre) it is found that the



solutions containing only 0.8% water have a higher degree of ionisation than those containing 6.2% of water.

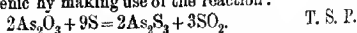
Curves are also given showing the relationship between degree of ionisation and amount of water present for solutions containing respectively 0.2, 0.5, and 1.0 mol. of acid per litre.

With the 1.0 mol. solution, the addition of water first diminishes and then increases the degree of ionisation. The somewhat abnormal values obtained when only small amounts of water are present are attributed to the existence of a hydrate,  $H_2SO_4 \cdot H_2O$ . J. J. S.

**Atomic Weight of Tellurium.** WILLY MARCKWALD and A. FOIZIK (*Ber.*, 1910, 43, 1710—1721).—From determinations of the loss of weight of telluric acid when converted into tellurium dioxide, Marckwald has previously deduced the atomic weight of tellurium to be 126.85 (*Abstr.*, 1908, ii, 33), which number is considerably lower than that usually accepted (127.5). The authors have further investigated the matter, using as the material, tellurium dioxide prepared from telluric acid, which had been recrystallised several hundred times. The tellurium dioxide was analysed volumetrically, being oxidised to telluric acid by potassium permanganate, and the excess of the latter determined by means of oxalic acid. The reaction was carried out either by Brauner's method (*Trans.*, 1891, 50, 250) in alkaline solution, or by Gooch and Howland's method (*Abstr.*, 1895, ii, 30) in acid solution. The method of Norris and Fay (*Abstr.*, 1898, ii, 404), in which the excess of permanganate is determined iodometrically, was also used, being modified, however, by the addition of sodium acetate in order to prevent the reversible reaction between telluric and hydriodic acids taking place. The method of Gooch and Peters (*Abstr.*, 1900, ii, 45) was found to be unsatisfactory.

The mean result for the atomic weight of tellurium is 127.61. Marckwald's abnormal results (*loc. cit.*) are accounted for by assuming that the telluric acid ( $H_2TeO_4 + 2H_2O$ ) used contained a small quantity of a higher hydrate in solid solution.

The authors have not been able to obtain satisfactory results with the method of Baker and Bennett (*Trans.*, 1907, 91, 1849), in which a mixture of tellurium dioxide and sulphur is heated in a current of nitrogen, whereby the dioxide is reduced to tellurium, and the sulphur oxidised to dioxide. It is shown that some sulphur trioxide is also formed. This formation of sulphur trioxide may account for the bad results obtained by Berzelius in the determination of the atomic weight of arsenic by making use of the reaction:



[Methods of Demonstrating the Properties of Liquid Air; the Collection of Atmospheric Nitrogen; and the Action of Sodium on Water.] H. REBENSTORFF (*Zeitsch. Physik.-chem. Unterr.*, 1910, 23, 28—32, 39—40, 43—44).—An account of methods employed by the author for demonstrating the properties of liquid air; collecting atmospheric nitrogen by passing air over heated magnesium with formation of magnesium nitride; and a sketch with description of the action of sodium when placed on wet blotting paper under a bell jar. F. M. G. M.

**New Compounds of Nitrogen with Metals and their Stability in the Light of the Periodic System.** FRANZ FISCHER and FRITZ SCHNÖRER (*Ber.*, 1910, 43, 1465—1479).—The method used was the formation of an arc between a silver anode and a cathode of the metal to be investigated; the electrodes were immersed in a liquid mixture of 90% argon and 10% nitrogen. The nitrides are formed by the interaction at high temperatures of the metallic vapours in the arc with nitrogen, and are preserved by the sudden cooling in the liquid gases.

The nitrides obtained were those of sodium, potassium, rubidium, cadmium, indium, thallium, lead, arsenic, antimony, tellurium, manganese, zinc, mercury, tin, and bismuth; of these, only the last five have been prepared previously. They are all true nitrides, and not derivatives of hydrazoic acid. They were never obtained quite pure, in most cases being contaminated by excess of the disintegrated metal and thereby coloured black. In the case of antimony nitride, evidence was obtained that it has the formula  $\text{SbN}$ . In all cases treatment with acids gave ammonium salts, no hydrazine salts or such like being formed.

The nitrides of metals with high atomic weights, for example, those of cadmium, mercury, lead, and bismuth, are explosive. The others decompose on careful heating, either with a slight puff, or else quietly.

With an arc discharge in gaseous nitrogen, zinc, cadmium, lead, bismuth, and nickel do not form nitrides. Tin and antimony give only traces of nitrides, whereas manganese readily forms the nitride (compare Arons, *Abstr.*, 1900, ii, 143).

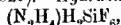
With the exception of the first group of the Periodic System, where exceptions occur, the left-hand columns of each group contain only metals which form nitrides stable at room temperature; the right-hand columns contain only metals which give nitrides that are unstable at room temperature and are decomposed either by shock or by heating. Gold, nickel, cobalt, and the platinum metals do not appear to form nitrides.

T. S. P.

**Solid Hydrates of Ammonia.** II. FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1910, 32, 748—749).—In an earlier paper (*Abstr.*, 1909, ii, 726) the freezing-point curve was given for the system ammonia-water which proved the existence of two hydrates:  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and  $2\text{NH}_3 \cdot \text{H}_2\text{O}$ . The work has now been repeated with additional precautions to ensure accuracy, and the results of the previous work are confirmed. The eutectic points are:  $\text{H}_2\text{O}-\text{NH}_3 \cdot \text{H}_2\text{O}$  (not determined);  $\text{NH}_3 \cdot \text{H}_2\text{O}-2\text{NH}_3 \cdot \text{H}_2\text{O}$ ,  $-87^\circ$ , with 56.5%  $\text{NH}_3$ ; and  $2\text{NH}_3 \cdot \text{H}_2\text{O}-\text{NH}_3$ ,  $-94^\circ$ , with 80%  $\text{NH}_3$ .

E. G.

**Hydrazine Silicofluoride and Hydrazine Titanofluoride.** ERICH FÄHLER and E. SCHOTT (*J. pr. Chem.*, 1910, [ii], 81, 552—556. Compare *Abstr.*, 1908, ii, 1029).—*Hydrazine silicofluoride*,



m. p.  $186^\circ$  (decomp.), is precipitated by the addition of alcohol to a mixture of equal molecular quantities of 50% aqueous hydrazine

hydrate and 20% silicofluoric acid. It is easily soluble in water, and yields silicon tetrafluoride and hydrazine dihydrofluoride (Abstr., 1891, 263) when distilled in a vacuum.

*Hydrazine titanofluoride*,  $(N_2H_5)_2TiF_6 \cdot 2H_2O$ , is prepared by dissolving titanium dioxide in cold fuming hydrofluoric acid in the proportions required to form titanofluoric acid, adding 50% aqueous hydrazine hydrate until the mixture is just alkaline, and evaporating the clear solution in a vacuum over sulphuric acid.

C. S.

**Oxidising Action of Ultra-violet Light on Gases.** Per. oxidation of Oxides of Nitrogen and Sulphur. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, 150, 1517—1520. Compare this vol., i, 349).—Nitrogen and oxygen do not combine under the influence of light from a quartz-mercury lamp. Nitrous and nitric oxides are decomposed into their elements, but in each case a portion of the gas unites with oxygen to form higher oxides. A mixture of nitrous oxide and oxygen behaves in a similar fashion.

When 2.38 c.c. of sulphur dioxide were exposed over mercury for three hours to the action of the lamp (110 volts), a contraction of 0.18 c.c. was observed, and the mercury became encrusted with a sulphate, sulphur being deposited on the sides of the tube. A mixture of sulphur dioxide and oxygen behaved in the same way, sulphur being deposited, although oxygen remained in excess. W. O. W.

**Application of the Laws of Eutectics to Definite Chemical Compounds.** ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 428—434).—The author has applied Flawitzky's law concerning eutectic alloys (Abstr., 1906, ii, 152) to the following cases of definite chemical compounds.

(1)  $PNCl_2$  forms a number of polymerides. Assuming that  $(PNCl_2)_2$  represents a eutectic compound of the two neighbouring polymerides, thus:  $(PNCl_2)_4 + (PNCl_2)_6 = 2(PNCl_2)_5$ , the equation  $n_0 = \sqrt{pM_1T_1} / \sqrt{qM_2T_2}$  (*loc. cit.*) gives the value 0.9553 instead of 1 for the ratio between the number of mols. of  $(PNCl_2)_4$  and  $(PNCl_2)_6$  present in the eutectic compound  $(PNCl_2)_5$ . The above equation gives the m. p.'s 133° and 62° respectively for the unknown polymerides  $(PNCl_2)_4$  and  $(PNCl_2)_6$ .

(2) Flawitzky's equation is also in agreement with the view that  $PI_3$  is a eutectic compound formed from  $P_2I_4$  and  $I_2$  according to the equation:  $P_2I_4 + 2I = 2PI_3$ , the two constituents being polymerised to the same degree. Similar agreement is found for the cases represented by the equations: (3)  $2NS + 3S = N_2S_3$ , the components being equally polymerised; (4)  $N_2H_4 + H_2O = N_2H_4 \cdot H_2O$ , the components being polymerised in the ratio  $(H_2O)_2 : N_2H_4$ ; (5)  $AsI_3 + 2I = AsI_5$ , where the relative polymerisation of the constituents is represented by

$$(AsI_3)_2 : (I)_3;$$

6)  $Te + TeCl_4 = 2TeCl_2$ , the relative polymerisation being

$$(Te)_2 : (TeCl_4)_5;$$

7)  $SbI_3 + 2I = SbI_5$ , the constituents being polymerised in the eutectic

compound, thus,  $(\text{SnI}_3)_2$ ; it is evident that if arsenic and antimony tri-iodides form a eutectic alloy, the latter should contain them in the proportions  $(\text{AsI}_3)_5 : (\text{SbI}_3)_3$ ; (8)  $\text{P}_2\text{S}_5 + 3\text{PCl}_5 = 3\text{PSCl}_3$ , where the relative polymerisation of the components is represented by  $(\text{P}_2\text{S}_5)_6 : (\text{PCl}_5)_3$ .

T. H. P.

**The Reciprocal Transformations of Ortho-, Pyro-, and Meta-phosphoric Acids on Heating.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1910, 67, 234—241).—The formation of pyrophosphoric acid as the first product of the dehydration of orthophosphoric acid is due to the presence of the double molecule  $(\text{H}_3\text{PO}_3)_2$ . The temperatures at which pyro- and meta-phosphoric acids are formed may be raised by increasing the pressure of water-vapour in contact with the acid. If the temperature reaches that at which the double molecules of orthophosphoric acid dissociate, the meta-acid should be formed directly without the production of pyrophosphoric acid.

The acid is heated in a platinum vessel, and air is passed through the apparatus, the proportion of water vapour being regulated by bubbling the air through sulphuric acid or water at a fixed temperature. With an increasing proportion of water-vapour, the temperature at which the pyro-acid is formed increases more rapidly than that of the meta-acid, but it is not found practicable to follow the two curves to their intersection, on account of the volatility of metaphosphoric acid at high temperatures.

C. H. D.

**Action of Air on Coal.** P. MAHLER (*Compt. rend.*, 1910, 150, 1521—1523. Compare Boudouard, *Abstr.*, 1909, ii, 234).—When air is passed over dry coal, free from occluded gases, at 25—30°, water, carbon dioxide, and carbon monoxide are slowly produced, the amount increasing as the temperature is raised. Less carbon monoxide is formed if the coal contains moisture. At 125°, the condensed water contains traces of hydrocarbons, and at 150° has acquired an odour of acetic acid.

W. O. W.

**Action of Heat on Carbon Monoxide from a Geological and Chemical Standpoint.** ARMAND GAUTIER (*Compt. rend.*, 1910, 150, 1383—1388).—Volcanic gases contain hydrogen, nitrogen, carbon monoxide, carbon dioxide, water, hydrogen sulphide, hydrogen chloride, ammonia, and methane.

On account of the dissociative action of heat, carbon dioxide, water, hydrogen chloride, and hydrogen sulphide cannot come from any great depth as such. All lavas contain ferrous silicate, which at its melting point (1250—1300°) is able to reduce water to hydrogen and carbon dioxide to monoxide. Whether hydrogen and carbon monoxide interact to give methane, and whether direct union of hydrogen and nitrogen yields ammonia, or whether metallic carbides and nitrides are the source of the methane and ammonia cannot be decided. With the object of throwing light on the question of whether carbon can exist in the pyrosphere of the earth as carbon monoxide, the author has re-examined the action of heat on carbon monoxide alone.

According to Deville (1864), carbon monoxide is partly dissociated at a bright red heat into carbon dioxide and carbon, whereas Berthelot (1891), and also Lothian Bell (1891), found that, although carbon dioxide was formed, even at  $550^{\circ}$ , no trace of carbon deposit could be observed. Berthelot supposed that a volatile carbon suboxide, such as  $C_3O$ , was produced. The author shows that carbon monoxide, as prepared by Berthelot from its compound with cuprous chloride, yields, not only carbon dioxide, but also water on heating at  $820^{\circ}$  and  $1250^{\circ}$ . Berthelot's monoxide therefore contained hydrogen, and the carbon unaccounted for in his experiments was probably in the form of a hydrocarbon. No suboxide of carbon of the kind which might produce oxalic acid, glycollic acid, or glyoxal could be detected. Deville's observations of the deposition of carbon could be repeated when traces of organic matter or ferric oxide were present. The author draws the conclusion that pure carbon monoxide is not appreciably dissociated at the melting point of lava under normal pressure. R. J. C.

**Action of Ozone on Carbon Monoxide.** PAUL CLAUSWANN (*Compt. rend.*, 1910, 150, 1332—1333. Compare Berthelot, *Compt. rend.*, 1879, 88, 50).—Remsen and Southworth (*Ber.*, 1875, 8, 1414) were unable to detect the formation of carbon dioxide when ozone acts on carbon monoxide in sunlight; by passing the mixed gases through a solution of barium hydroxide, however, an abundant precipitate of barium carbonate is produced. The oxidation of carbon monoxide by ozone takes place in darkness, but more rapidly in daylight. Traces of water-vapour accelerate the reaction. W. O. W.

**Preparation of Pure Argon and Nitrogen.** FRANZ FISCHER and OTTO HÄRNEL (*Ber.*, 1910, 43, 1435—1442).—A special apparatus is described for the purification of crude argon (obtained by the action of calcium carbide on air: Abstr., 1908, ii, 688) from gases other than those of the argon group. With the exception of two iron tubes, containing calcium and copper oxide respectively, and heated in furnaces, the apparatus is made entirely of glass, all joints being fused together. Special stopcocks and stoppers with mercury seals are used, and also a special arrangement for connecting the glass parts with the iron tubes, so that no air can penetrate into the apparatus from the outside. The gas is kept automatically circulating round the apparatus, nitrogen being absorbed by the calcium, and hydrogen and carbon monoxide oxidised by the copper oxide; there are the usual absorbents for moisture and carbon monoxide.

The apparatus may also be used for purifying nitrogen, the calcium being then replaced by copper turnings.

The density of crude argon, purified in the above apparatus was 19.945, agreeing with the value (19.940) obtained by Ramsay and Travers; that of nitrogen was 14.018.

During the circulation of the argon, intensive phosphorescent effects were noticed, being the more pronounced the purer the argon. No such effects were observed in the case of nitrogen. T. S. P.

**New Experiments on the Combining Capacity of Argon.** FRANZ FISCHER and FRITZ SCHRÖTER (*Ber.*, 1910, 43, 1442—1454).—The apparatus used by Fischer and Ilievici (Abstr., 1908, ii, 1034;

1909, ii, 139, 232) for the production of an arc in liquid argon has been improved so that it is perfectly gas-tight; it retained the highest vacuum for forty-eight hours, and after working with it for a year the argon used remained quite pure. Special arrangements were also devised for regulating the distance apart of the electrodes; for under-cooling the liquid air used to condense the argon in such a way that fractional distillation of the nitrogen did not take place, and for maintaining an arc between metals which either did not disintegrate or only disintegrated with difficulty.

Experiments were carried out with forty-five metals, using argon purified according to the method described in the previous abstract. Some of the metals disintegrated with the formation of a black powder (see succeeding abstract), but the majority did not disintegrate. With the exception of Groups I and VII of the Periodic Table, the metals which did not disintegrate are contained in the left-hand column (sub-group) of each group, the metals in the first two horizontal rows being counted as belonging to the left-hand column. The metals which disintegrated are those in the right-hand column. None of the metals of the platinum and iron groups disintegrated, those investigated being iron, cobalt, nickel, palladium, iridium, and platinum.

When the metal did not disintegrate, the arc formed consisted of incandescent argon, and had a very high resistance; it was also rich in ultra-violet rays.

T. S. P.

**Modifications of Metals Resulting from Electrical Disintegration in Liquid Argon.** FRANZ FISCHER and FRITZ SCHRÖTER (*Ber.*, 1910, 43, 1454—1464).—When an arc discharge takes place between metal electrodes in pure liquid argon, compounds with argon are not formed. In no case could it be proved that they have a momentary existence, even at the temperature of liquid air. If it does so happen that they exist, they must be far more explosive than cadmium nitride.

Owing to the disintegration, a number of metals were obtained in a new form. Lithium and sodium were obtained as brown, and potassium, rubidium, and caesium as blue, relatively stable powders. The lithium powder had a density approximately the same as that of liquid argon ( $D=1.2$ ); at  $20^{\circ}$  lithium has  $D=0.534$ , so that the density increases enormously when the temperature falls to  $-186^{\circ}$ . Zinc and cadmium gave deep black modifications, which were only stable at the temperature of liquid air. Mercury gave a black powder which dissolved in the excess of mercury when the temperature rose.

Copper did not disintegrate, silver only to a very slight extent, and gold slightly more than silver. The disintegrated gold was dark brown by reflected, and green by transmitted light.

Zinc, tin, indium, and manganese gave pyrophoric powders. Bismuth gave a deep black powder, which gradually became grey, and at the same time more dense at room temperature, denoting a change from the amorphous to the crystalline form. Arsenic and antimony gave black powders which did not contain any of the yellow modifications,

although the experiments were carried out under exclusion of day-light.

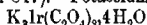
None of the finely divided powders obtained absorbed argon at room temperature; in the case of zinc, adsorption did not occur even at the temperature of liquid air. This is in marked contrast with the behaviour of finely divided charcoal.

T. S. P.

The Liberation of Helium from Minerals by the Action of Heat. D. ORSON WOOD (*Proc. Roy. Soc.*, 1910, *A*, 84, 70—78).—The minerals were heated in Jena glass tubes (up to 750°) and in quartz tubes (up to 1200°), and the total volume of helium liberated was measured. For monazite very little of the helium came off when the temperature was maintained at 500°, but above this temperature the evolution was more rapid, although even at 720° it did not reach a limit after very prolonged heating. At 900° to 1200° the greater part of the helium present came off in the first day. For thorianite a practical limit could be reached at each temperature, and was found to be 0.7% at 300° after five hours, 8.5% at 500° after eighty hours, 62.3% at 750° after three hundred and twenty hours, and the whole at 1000° after thirty hours. The laws governing the liberation of gas agree with the view that a small proportion of the gas exists diffused through the mineral, and that most of it is concentrated in minute cavities within it. The pressure of helium in a thorianite crystal at 0° must be very great, possibly above 200 atmospheres.

F. S.

Crystallography of Some Inorganic Compounds. FERRUCCIO ZAMBONINI (*Zeitsch. Kryt. Min.*, 1910, 47, 620—629).—Details respecting the following salts are given. Potassium thioarsenate,  $K_2SnS_3 \cdot 3H_2O$  (cubic,  $D^{18}$  1.847). Potassium iridium oxalate,



(triclinic,  $a:b:c=0.7319:1:0.9565$ ;  $\alpha=88^\circ 34'$ ,  $\beta=94^\circ 30'$ ,  $\gamma=57^\circ 1'$ ,  $D^{19}$  2.510). Silver iridium oxalate,  $Ag_3Ir(C_2O_4)_3 \cdot 3H_2O$  (monoclinic,  $a:b:c=1.2760:1:0.8345$ ;  $\beta=114^\circ 43'$ ). Copper dichromate,  $CuCr_2O_7 \cdot 1$  or  $2H_2O$  (triclinic,  $a:b:c=0.6133:1:0.5117$ ;  $\alpha=67^\circ 2'$ ,  $\beta=125^\circ 14'$ ,  $\gamma=111^\circ 26'$ ,  $D^{19}$  2.286). Tetramethylammoniumiron nitrosulphide,  $[Fe_4(NO)_7S_3]NMe_4$  (triclinic,  $a:b:c=0.8648:1:1.3125$ ;  $\alpha=87^\circ 29\frac{1}{2}'$ ,  $\beta=106^\circ 7'$ ,  $\gamma=93^\circ 44'$ ,  $D^{19}$  2.056). Tetraethylammoniumiron nitrosulphide,  $[Fe_4(NO)_7S_3]NEt_4$  (triclinic,  $a:b:c=1.0221:1:1.0247$ ;  $\alpha=85^\circ 8'$ ,  $\beta=97^\circ 8'$ ,  $\gamma=99^\circ 17\frac{1}{2}'$ ,  $D^{19}$  1.883). Glucinum sulphate,  $GlSO_4 \cdot 6H_2O$  (cubic).

L. J. S.

The Behaviour of Lithium towards Sodium, Potassium, Tin, Cadmium, and Magnesium. G. MASING and GUSTAV TAKMANN (*Zeitsch. anorg. Chem.*, 1910, 67, 183—199).—The alloys are melted in quantities of only one or two grams in Jena glass tubes, or, for high temperatures, in iron tubes, in an atmosphere of hydrogen, which does not react rapidly with lithium below 400°. The thermocouple is of fine wires, protected by a capillary of Jena glass.

Lithium melts at 179°. It is only very slightly miscible at its melting point with sodium or potassium. Glass is wetted by molten lithium, but not by sodium, so that the boundary between the two

metals is a meniscus. Lithium and tin form three compounds:  $\text{Li}_3\text{Sn}$ , forming a maximum on the freezing-point curve at  $680^\circ$ ;  $\text{Li}_2\text{Sn}_2$ , forming a flat maximum at  $465^\circ$ ; and  $\text{Li}_2\text{Sn}_3$ , reacting with the melt at  $330^\circ$ . The freezing-point curve of alloys of lithium and cadmium has a maximum at  $541^\circ$ , corresponding with the compound  $\text{LiCd}$ , and a break at  $505^\circ$ , indicating a possible compound,  $\text{LiCd}_2$ . Lithium and magnesium appear to form solid solutions, but at the temperature of fusion the alloys attack the glass sheath of the thermocouple. The elements of the alkali and zinc groups are compared with respect to their power of forming compounds.

C. H. D.

**The Electrolytic Preparation of Rubidium.** GEORG VON HEVESY (*Zeitsch. anorg. Chem.*, 1910, 67, 242—247).—Rubidium is the only alkali metal that has not hitherto been prepared electrolytically. Rubidium hydroxide (100 grams) is melted in a nickel vessel, and the iron cathode wire and iron anode cylinder are surrounded by magnesite cylinders. The cathode cylinder is closed above, except for a small opening for the escape of the hydrogen which is formed at first. After a few minutes, this opening is closed with magnesite. The nickel vessel is rapidly cooled after the electrolysis, the mass of hydroxide is broken, and the cylinder containing the rubidium is opened under pyridine cooled by a freezing mixture. The yield is 30% after three-quarters of an hour, using a current of 5 amperes. Part of the loss is due to the readiness with which oxygen is absorbed by the hydroxide, and thus conveyed to the cathode. The solubility of rubidium in its hydroxide is only small, but the reaction  $\text{RbOH} + \text{Rb} = \text{Rb}_2\text{O} + \frac{1}{2}\text{H}_2$  is perceptible at  $360^\circ$ . The absorption of heat in this reaction decreases in the series Na-K-Rb-Cs.

Rubidium hydroxide has  $D_{20}^{25} 3.203$ , and m. p.  $301^\circ \pm 1^\circ$ .

Alloys of rubidium with potassium and sodium are obtained by the action of these metals on rubidium hydroxide.

C. H. D.

**Some Complex Metallic Cations.** WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, 67, 248—249).—If a solution of a silver salt is run into a solution of ammonia, the point at which a permanent precipitate is produced is readily observed, and the formula of the complex cation may be deduced. The formulae  $\text{Ag}(\text{NH}_3)_2$ ,



and  $\text{Ag}(\text{NH}_2\text{Et})_2$  are thus obtained, in agreement with the results of other methods. When copper sulphate and ammonia are employed, the end-point is less sharp, but the titrations indicate the formula  $\text{Cu}(\text{NH}_3)_4$ . Sharp results are not obtained with zinc, cadmium, or nickel.

C. H. D.

**Nature of Schaum's Substance B.** A. P. H. TRIVELLI (*Chem. Weekblad*, 1910, 7, 381—387. Compare Schaum, *Zeitsch. Elektrochem.*, 1908, 14, 483).—Schaum's substance B is a silver halide which is more soluble than the corresponding silver halide which has not been exposed to light. It, and not the original silver halide, is the starting point of the author's series of photochemical decompositions.

A. J. W.



**The Solubility of Sparingly Soluble Silver Salts.** G. STAFFORD WHITBY (*Zeitsch. anorg. Chem.*, 1910, 67, 107—109).—The solubility of very sparingly soluble silver salts has hitherto been determined by physical methods. The analytical method described by the author (this vol., ii, 654) enables a chemical determination to be made. The solubilities of the arsenate, arsenite, bromate, chloride, chromate, ferricyanide, iodate, oxalate, oxide, and thiocyanate are given. A litre of water dissolves 0.00154 gram of silver chloride at 21°, but 0.0217 gram at 100°; the precipitate should therefore not be washed with boiling water in accurate work. One % of hydrochloric acid diminishes the solubility of silver chloride, but further additions increase it, so that the solubility in 5% hydrochloric acid is greater than in water. The solubility of silver chromate does not diminish with rising temperature, as supposed by Abegg and Cox (*Abstr.*, 1904, ii, 256). The solubility of the oxide increases with time, only becoming constant after fourteen days.

C. H. D.

**Colloidal State of Calcium Carbonate.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 266).—Chalk (containing calcium sulphate) was washed by decantation during eleven days. When the washed calcium carbonate was filtered from the last wash-water, it was always observed that the filtrate was slightly turbid. If, however, this liquid, after ten minutes, was re-filtered, a clear filtrate was obtained. The conclusion is drawn that calcium carbonate can exist in the colloidal state, although for only a short time.

E. H.

**Action of Alkali Nitrates on Strontium Carbonate.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 162—164).—It has been shown previously (this vol., ii, 411) that under certain conditions calcium or barium, but not strontium, carbonate is attacked by boiling sodium nitrate solution. It is found, however, that a small amount of strontium nitrate is formed when a mixture of strontium carbonate (1 part) and sodium nitrate (2—3 parts) is either heated gradually to redness and kept at this temperature for ten minutes, or heated at 325° for twenty minutes. Moreover, if a solution of potassium nitrate (75 grams) in water (100 c.c.), containing strontium carbonate (10 grams), is heated on a water-bath for thirty-two hours, the filtrate is found to contain a small, although quite definite, amount of strontium in solution.

E. H.

**Barium Sulphate.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 267).—Barium sulphate was precipitated from very dilute solutions in two tubes. One of the latter was kept in comparative darkness, the other was exposed to sunlight during several hours per day for fourteen months. The barium sulphate exposed to sunlight polymerised slightly more rapidly, and formed a granular precipitate. In the unexposed tube the particles of barium sulphate the precipitate were appreciably smaller than the others.

E. H.

**The Reversible Action of Oxygen on Magnesium Chloride.**  
 WILHELM HIRSCHKIND (*Zeitsch. anorg. Chem.*, 1910, 67, 113—148).—The equilibrium between oxygen and magnesium chloride, or between chlorine and magnesium oxide, has been investigated by Haber and Fleischmann, and by Moldenhauer (Abstr., 1907, ii, 84, 85). Their experiments have now been repeated with increased precautions.

Passing the gas over the heated solid and analysing the issuing gases, it is found that when chlorine acts on magnesium oxide or on a mixture of equal parts of oxide and chloride, the correct value for the equilibrium is obtained. From the other side, a mixture of chlorine and oxygen, containing only slightly less than the equilibrium proportion of chlorine, gives a nearly correct value when passed over the mixed solids, but when a mixture richer in oxygen is used, the evolution of chlorine is always low. It is uncertain whether this difference is due to the formation of an oxychloride.

A second apparatus is described for making statical experiments, the solid being left in contact with a prepared mixture of gases for a given time at a given temperature. It is found that whilst the equilibrium is attainable from both sides, the prolonged passage of gas leads to a new apparent equilibrium, corresponding with a much lower pressure of chlorine. This effect appears to be due to the formation of an oxychloride, and there is also evidence for the absorption of chlorine by finely divided magnesium oxide.

The values of  $k_p = p_{\text{Cl}_2}/p_{\text{O}_2}$  found are: by the statical method, at 621°, 2.53; at 665°, 2.97; and at 714°, 3.4. The value obtainable from both sides by the dynamical method is, at 665°, 3.18. The heat developed by the reaction  $\text{MgCl}_2 + \frac{1}{2}\text{O}_2 = \text{MgO} + \text{Cl}_2$  is about 6000 cal., within the range investigated. The calculation of the theoretical value is uncertain, as the specific heats of the reacting solids at different temperatures are unknown.

C. H. D.

**Crystalline Form and Composition of the Hydrated Magnesium Carbonate prepared by Moressée.** Its Relation to Landsfordite. GUISEPPE CESÀRO (*Bull. Acad. roy. Belg.*, 1910, 234—265).—Moressée has shown (*Ann. Soc. géol. Belg.*, 37, 151—156) that when the mixture of calcium and magnesium oxides, obtained by calcining dolomite, is powdered, suspended in water at 10°, and the liquid saturated with carbon dioxide under a pressure of 5—6 atmospheres, only the magnesium oxide is dissolved. The filtrate deposits crystals, the composition of which is found by the author to correspond with  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ , although in some cases a somewhat higher percentage of magnesia is found, probably owing to partial decomposition.

The crystals obtained by Moressée are monoclinic [ $a:b:c = 1.6323:1.096676, \beta = 77^\circ 50' 58''$ ], the general form being an hexagonal prism. The three principal birefringences are  $n_g - n_p$  51,  $n_p - n_m$  38,  $n_m - n_p$  13. The crystals are harder than gypsum, but softer than Iceland spar; they have  $D^{20}$  1.73. The crystalline form is practically identical with that of landsfordite. It is suggested that Moressée's carbonate is identical with the latter mineral, the smaller proportion of carbon dioxide (Dana gives  $4\text{MgO} \cdot 3\text{CO}_2 \cdot 22\text{H}_2\text{O}$  as

representing the composition of landefeldite) being due to decomposition on analysis.

Moresée's carbonate is soluble in 267 parts of cold water, the solution being alkaline to both litmus and phenolphthalein. The residue obtained by the spontaneous evaporation of its aqueous solution seems to contain both the original substance and a small quantity of nesquehonite,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ . A solution of Moresée's carbonate becomes turbid when heated to boiling, but the precipitate redissolves on cooling the liquid to  $10^\circ$ , and the latter, when evaporated, leaves an amorphous residue containing crystals of both  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$  and of nesquehonite.

When the solution of magnesia obtained technically by Moresée is boiled, a precipitate is formed having the composition corresponding with  $4\text{MgO} \cdot 3\text{CO}_2 \cdot 14 \cdot 6\text{H}_2\text{O}$ , but if heated at  $40\text{--}50^\circ$  on a water-bath, a crystalline deposit of rectangular needles is produced, which contains nesquehonite, but no trace of the pentahydrated carbonate.

E. H.

Oxychlorides of Zinc. DRIOT (*Compt. rend.*, 1910, 150, 1426—1428. Compare Schindler, *Ann. Mag. Pharm.*, 1831, 36, 45; Kane, *Ann. Chim. Phys.*, 1839, [ii], 2, 72; Mailhe, *Abstr.*, 1901, i, 601).—Determinations of the solubility of zinc oxide in an aqueous solution of zinc chloride indicate the existence of two oxychlorides having the composition  $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$ , and  $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1 \cdot 5\text{H}_2\text{O}$ . These have been isolated and analysed. The first is amorphous and loses  $5\text{H}_2\text{O}$  at  $200^\circ$ , whilst the latter forms microscopic crystals, losing  $1\text{H}_2\text{O}$  at  $230^\circ$ , and decomposing at a higher temperature. A study of the equilibrium in systems containing these oxychlorides with zinc chloride in aqueous solution has shown that the composition of these substances does not vary with temperature. No evidence has been obtained for the existence of eight oxychlorides described by previous observers.

W. O. W.

Zinc Hydrazide and a General Method for the Preparation of Metal Hydrazides. ERICH EULER and R. L. KRAUSE (*Ber.*, 1910, 43, 1690—1695. Compare *Abstr.*, 1909, ii, 234).—When hydrazine and zinc ethyl dissolved in dry ether interact, a colourless precipitate is formed, which ignites spontaneously when it comes in contact with the air. This has approximately the composition  $\text{ZnN}_2\text{H}_4$ . The same zinc hydrazide is formed from zinc diamide,  $\text{Zn}(\text{NH}_2)_2$ , and anhydrous hydrazine in ethereal suspension. The anhydrous diamides of other metals react with hydrazine in a similar manner, forming hydrazides which ignite spontaneously in the air.

E. F. A.

A Supposed Allotrope of Lead. ERNST COHEN and KATSUJI INOUE (*Chem. Weekblad*, 1910, 7, 454—458. Compare Lehmann, *Abstr.*, 1890, 437).—Measurements of the *E.M.F.* between the forms of lead obtained by Lehmann by the electrolysis under certain conditions of solutions of lead salts have proved that these forms are not allotropic modifications of lead, but are identical.

A. J. W.

Analysis of Some Bolivian Bronzes. MORRIS LOEB and S. R. MOREY (*J. Amer. Chem. Soc.*, 1910, 32, 652—653).—Analyses are given

of six specimens of various native bronze implements: (1) copper 91.81, tin 7.56; (2) copper 90.51, tin 8.92; (3) copper 95.59, tin 4.48; (4) copper 97.43, arsenic 2.14; (5) copper 94.96, tin 4.98, sulphur 0.53; (6) copper 91.43, tin 7.05.

Approximate densities: (1) 8.68, (2) 8.94, (3) 8.92, (4) 8.83, (5) 8.61, (6) 8.18(?)

The complete absence of silver points to the tin being obtained from cassiterite rather than native tin.

L. DE K.

**Preparation of Mercuric Chloride from Mercuric Sulphate and Sodium Chloride by the Wet Process.** ERWIN RUPP and W. KLEE (*Apoth. Zeit.*, 1910, No. 26. Repriot, 3 pp.).—One hundred parts of mercuric sulphate are mixed with 40 parts of common salt, well powdered, and then moistened with 20 parts of 5% hydrochloric acid. The mass is frequently stirred, and, after twenty-four hours, extracted with 95% alcohol in a suitable extraction apparatus. The alcohol is recovered by distillation, and the product recrystallised from boiling water. The yield is about 90%.

Mercuric nitrate solution should be converted into chloride by addition of a sufficiency of sodium chloride, and then carefully neutralised if it is desired to precipitate the mercury as sulphide.

L. DE K.

**Nitrides and Oxides from Aluminium Heated in Air.** J. O. SERPEK (*Compt. rend.*, 1910, 150, 1520—1521. Compare Kohn-Abrest, this vol., ii, 506).—Some of the observations made by Kohn-Abrest had already been recorded (Fichter, *Abstr.*, 1907, ii, 691; Bronnert, *Bull. Soc. Ind. Mulhouse*, 1909). The author has been unable to obtain a nitride differing from AlN in composition, as described by Kohn-Abrest.

W. O. W.

**Adsorptive Power of Hydroxides of Silicon, Aluminium, and Iron.** IV. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1910, 67, 110—112; *Biochem. Zeitsch.*, 1910, 25, 420—424. Compare this vol., ii, 104).—Talc and steatite, like clay, have the power of adsorbing colloids (soap, starch, dextrin) and complex dyes, such as aurin, fluorescein, and cochineal, whilst acids and salts are not adsorbed.

G. H. D.

**Formation of Basic Aluminium Sulphate when Zinc Sulphate is Boiled with Alum.** O. SCHWEISSINGER (*Pharm. Zentral.*, 1910, 51, 493—494).—When a solution of 75 grams of zinc sulphate and 75 grams of alum in 1000 grams of water is boiled, a precipitate of basic aluminium sulphate begins to form after about ten minutes. Under the same conditions, a solution of aluminium sulphate gives no precipitate. Magnesium sulphate acts similarly to zinc sulphate; sodium or potassium sulphate has no effect.

T. S. P.

**Reactions of Artificial Zeolites.** ANTONY G. DOROSCHEWSKY and A. BARDT (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 435—442).—The

authors have investigated the influence of various conditions on the velocity with which an artificial sodium zeolite is attacked by salt solutions:  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, n\text{SiO}_2 + \text{RSO}_4 = \text{RO}, \text{Al}_2\text{O}_3, n\text{SiO}_2 + \text{Na}_2\text{SO}_4$ . The zeolite employed had the percentage composition:  $\text{SiO}_2$ , 42.06;  $\text{Al}_2\text{O}_3$ , 20.45;  $\text{Na}_2\text{O}$ , 12.10, and  $\text{H}_2\text{O}$ , 25.00, and was sieved so as to render it approximately uniform in size of grain.

The zeolite is attacked considerably more readily by an aqueous solution of calcium chloride containing an amount of calcium equivalent to the sodium of the zeolite than by a solution of similar concentration in 65% aqueous alcohol. That this variation in the velocity of the reaction is due to a difference in the extent to which the calcium chloride is dissociated in the two solutions is confirmed by the observation that the zeolite is not acted on by an aqueous solution of mercuric cyanide. In this action, the velocity is at first very great, but later gradually diminishes, a condition of equilibrium being attained only after a very considerable period of time. Rise of temperature is accompanied by marked increase in the rate of change, but the character of the velocity curve remains unaltered. Experiments with solutions of magnesium, calcium, strontium, and barium chlorides show that increase in the atomic weight of the metallic ion of the attacking salt results in increased velocity of the reaction; with magnesium chloride the action is very considerably slower than with the other three chlorides.

T. H. P.

**Production of Cementation Steel. VI. FEDERICO GIOLITTI and F. CARNEVALI** (*Atti. R. Accad. Sci. Torino*, 1910, 45, 376—387).—The authors have already given the results of experiments in which steels with low carbon contents (0.05—0.10%) were subjected to the carburising action of various gases (Abstr., 1909, ii, 240). The same method of experimenting has now been applied to two samples of steel containing (A) 0.18% C, 0.35% Mn, 0.05% Si, 0.07% P, and 0.05% S, and (B) 0.94% C, 0.90% Mn, 0.17% Si, 0.04% P, and 0.02% S. At 800° cementation is less intense for steel B than for the soft steel, support thus being given to the view that a considerable part is played by the phenomena of diffusion of the carbon owing to differences of concentration among the different portions of the mass of  $\beta$  or  $\gamma$  iron in which it is dissolved. When ethylene or methane is employed at either the ordinary or reduced (600 or 450 mm.) pressure, the hyper-eutectic zone is considerably deeper in steel B than in A. At 900° the second factor in the cementation process, that is, the diffusion of the carburising gas into the metallic mass, begins to play a preponderating part, and this is still more the case when carbon monoxide is employed; similar results are observed with illuminating gas rich in carbon monoxide, and, to a more marked extent, at a temperature of 1000°. At 1100° the differences in the course of the carburisation, due to the different initial concentrations of the carbon, are more distinct than at lower temperatures. Microphotographs render evident the accumulation of the cementite in the zone contiguous with the superficial eutectic stratum.

T. H. P.

**The Ternary System Iron-Copper-Nickel. RUDOLF VOGL** (*Zeitsch. anorg. Chem.*, 1910, 67, 1—16).—Iron and copper form two

limited series of solid solutions (Sahmen, Abstr., 1908, ii, 187), whilst nickel forms continuous series of solid solutions with both iron and copper (Guertler and Tammann, Abstr., 1905, ii, 528; 1907, ii, 174), thus the addition of nickel may be expected to reduce the gap in the mutual solubilities of iron and copper in the solid state. The limits are more readily determined by microscopical than by thermal methods, as the diffusion is slow in comparison with the rate of cooling, and it is therefore necessary to anneal for a long time after freezing in order to obtain equilibrium. The results are expressed in the form of a triangular diagram and of several vertical sections through the space model.

The limit of saturation of the ternary solid solutions is a curve starting from 96.5% Fe and 3.5% Cu, cutting the nickel diagonal at 40% Ni, and ending at 2.75% Fe and 97.25% Cu. All alloys falling outside this curve are homogeneous if sufficiently annealed. The alloy containing 72% Fe, 7% Cu, and 24% Ni has when etched with nitric acid a structure resembling that of martensite.

The unsaturated solid solutions of medium composition are exceedingly tough, the crystals being capable of great deformation without breaking. All the alloys are magnetic at the ordinary temperature.

C. H. D.

**Ultramicroscopical Studies. III. A Photochemical Reaction.** J. AMANN (*Chem. Zentr.*, 1910, i, 1117; from *Schweiz. Woch. Chem. Pharm.*, 1910, 48, 4-8, 24-28. Compare Abstr., 1909, ii 983, 1036).—The sensitiveness of certain alkali-iron salts of organic acids may be due, in different cases, to (1) simple decomposition of the double salt and reduction of ferric to ferrous iron (ferric ammonium oxalate); (2) reduction, accompanied by coagulation of the colloid and formation of a gel, the reaction being reversed in darkness (ferric potassium tartrate and ferric sodium pyrophosphate with sodium or ammonium citrate); (3) reduction of the iron and oxidation of the organic radicle, without the formation of a gel. The last case has not been observed. Only those double ferric salts are sensitive to light which contain a reducing group, principally HCOH. Substances which accelerate the coagulation retard the re-formation of a sol. The action of light on the colloidal complex is believed to be a hydrolysis forming ferric hydroxide and the organic acid, followed by reduction of the ferric iron.

C. H. D.

**Colloidal Character of the Chromopolysulphuric Acids.** PABLO MARTÍNEZ-STRONG (*Compt. rend.*, 1910, 150, 1172-1174; *Anal. Fis. Quím.*, 1910, 8, 199-202).—It is suggested that Recoura's chromopolysulphuric acids are negative colloids, since they are precipitated by almost all metallic salts, by acids, and by heat, but not by ammonia, and the precipitate appears to be the same in every case.

Examination of the acids with the ultramicroscope confirms this view, numerous brilliant particles being seen with characteristic Brownian motion.

After precipitation, 3, 4, or 5 molecules of sulphuric acid remain in

solution, and the precipitate has the composition  $\text{H}_2\text{Cr}_2(\text{SO}_4)_4$  (sulphochromic hydrate). It is uncertain whether the sulphuric acid is uncombined in the solid chromo-acids or is liberated when they are dissolved, or is only set free on precipitation by the salts, etc. Sulphochromic hydrate is obtained on heating either tetra-, penta-, or hexa-sulphochromic acids at  $140-150^\circ$ .

The author, adopting Duclaux's hypothesis of colloids (this vol., ii, 108), suggests that the sulphochromic hydrate constitutes the nucleus or micella of the colloid round which the remaining molecules of sulphuric acid are loosely aggregated in the intermicellar liquid.

The crystallisation of chromium sulphate in the violet form in presence of sulphuric acid is attributed to the hydrolating action of the latter.

R. J. C.

**Metallurgy of Uranium and Vanadium.** JUSTIN H. HAYNES (*Mines and Minerals*, 1909, 30, No. 3, 139-140).—The discovery of the mineral carnotite in West Colorado furnished the first example of the occurrence together of uranium and vanadium in workable quantities. At first the uranium only was extracted, but as the demand for vanadium increased, the problem of how to separate the two had to be considered. A recent method is founded on the fact that both the uranium and vanadium in carnotite are readily soluble in hot sodium carbonate, forming sodium uranium carbonate ( $2\text{Na}_2\text{CO}_3 \cdot \text{UO}_2 \cdot \text{CO}_3$ ) and sodium vanadate ( $\text{Na}_2\text{VO}_3$ ), thus separating them from calcium and iron. The uranium is then precipitated as sodium uranate ( $\text{Na}_2\text{O} \cdot 3\text{UO}_3$ ) with sodium hydroxide, and the vanadium subsequently separated from the filtrate as calcium vanadate [ $\text{Ca}_2(\text{VO}_3)_2$ ]; another modification was the formation of ferrous vanadate without the employment of lime, but it presented serious practical difficulties owing to the large quantity of colloidal slime which was formed.

In 1908, Fleck and Haldane patented a method in which the crushed ore is agitated with 15-20% sulphuric acid, and the acid solution containing the uranium, vanadium, iron, and copper brought into contact with fresh ore until neutral, when some of the required constituents will be precipitated upon it as basic sulphates or carbonates; the enriched ore is then treated with fresh acid, and the neutral solutions clarified by filtration; powdered limestone added until the uranium, vanadium, and copper fractions just commence to separate; the solution is then freed from calcium sulphate, and the required fraction completely precipitated by further treatment with limestone. The product (a complex mixture) may be dried, ignited, or else further purified by any of the known methods.

The author considers it improbable that any method involving the employment of sulphuric acid can be commercially successful.

F. M. G. M.

**Fluorine Salts of Vanadium.** N. COSTĂCHESCU (*Anu. Sci. Univ. Jassy*, 1910, 6, 117-123).—Ephraim (Abstr., 1903, ii, 418) has put forward the rule that in the series of complex salts formed from vanadium fluoride and the fluorides of the alkali metals, including ammonium, the greater the atomic weight of the alkali metal the

smaller is the number of molecules of the alkali fluoride contained in the salt. The author finds that this rule holds for the rubidium and cesium compounds, which, together with the potassium compound, are of the type  $\left[ \text{V} \begin{smallmatrix} \text{F}_4 \\ 2\text{H}_2\text{O} \end{smallmatrix} \right] \text{M}$ , containing only one molecule of the alkali fluoride. The alkali metal can be replaced by aniline, and the compounds still conform to this rule, since the salts then formed are  $[\text{VF}_6](\text{NH}_2\text{Ph})_3$  and  $\left[ \text{V} \begin{smallmatrix} \text{F}_5 \\ \text{H}_2\text{O} \end{smallmatrix} \right](\text{NH}_2\text{Ph})_2$ .

The salt  $[\text{VF}_6](\text{NH}_2\text{Ph})_3$  is formed by the crystallisation of a concentrated solution of vanadium trifluoride (1 mol.) in excess of aniline hydrofluoride (3 mols.); pale green crystals. The compound  $\left[ \text{V} \begin{smallmatrix} \text{F}_5 \\ \text{H}_2\text{O} \end{smallmatrix} \right](\text{NH}_2\text{Ph})_2$  results when 2 mols. of aniline hydrofluoride are used to 1 mol. of vanadium fluoride; green crystals.

The salts  $\left[ \text{V} \begin{smallmatrix} \text{F}_4 \\ 2\text{H}_2\text{O} \end{smallmatrix} \right] \text{M}$ , where M is either K, Rh, or Cs, are each obtained by mixing solutions of vanadium trifluoride and of the alkali fluoride in the proper proportions (1 mol. : 1 mol.) and evaporating if necessary.

T. S. P.

**Electrolytic Refining of Bismuth.** FRITZ FOERSTER and E. SCHWABE (*Zeitsch. Elektrochem.*, 1910, 16, 279—281).—In the electrolytic refining of lead, the anode mud contains bismuth, lead, and silver. It is found that this mixture can be separated electrolytically, using a solution of bismuth silicofluoride as electrolyte; the lead passes into solution, and silver remains undissolved. The potentials of lead and bismuth in solutions of their silicofluorides containing one equivalent per litre are +0.144 and -0.295 volt respectively (compared with the hydrogen electrode). Solutions containing as little as 26 grams of bismuth per litre give perfect deposits with 0.004 ampere per sq. cm. Stronger solutions and higher temperatures allow higher current densities to be used.

T. E.

**Halides of Tantalum.** WALTER K. VAN HAAGEN (*J. Amer. Chem. Soc.*, 1910, 32, 729—731).—Tantalalic bromide,  $\text{TaBr}_5$  (Rose, *Ann. Phys. Chem.*, 1856, [ii], 99, 87), can be prepared by passing bromine vapour over a strongly heated mixture of freshly ignited tantalio oxide and pure sugar-carbon, air having been previously removed by heating the mixture in a current of dry carbon dioxide. The salt crystallises in long, yellow plates, has m. p. about 240° and h. p. about 320°, can be sublimed in an atmosphere of hydrogen, fumes in moist air, and reacts readily with methyl or ethyl alcohol.

Neither Rose (*loc. cit.*) nor Moissan (Abstr., 1902, ii, 266) was able to obtain a tantalum iodide, but it has now been found that *tantalalic iodide*,  $\text{TaI}_5$ , can be prepared by heating the bromide in a current of hydrogen iodide; it sublimes in nearly black plates, melts to a dark brown liquid, can be distilled in a current of carbon dioxide, and fumes in moist air.

E. G.

**Tantalum Sulphide.** HEINRICH BILTZ and CARL KIRCHER (*Ber.*, 1910, 43, 1636—1645).—Tantalum sulphide has hitherto not been



prepared in a pure condition, so that the formula  $Ta_2S_5$ , which does not correspond with that of the oxide,  $Ta_2O_5$ , was doubtful. The author prepares the pure sulphide by passing a dry mixture of hydrogen sulphide and carbon disulphide over heated tantalum oxide. The oxide is attacked at  $650^\circ$ , but the pure sulphide is heat obtained at temperatures higher than  $900^\circ$ . It is stable at all events up to  $1300^\circ$ , and above  $1200^\circ$  it begins to change from the amorphous to the crystalline condition. The formula was found to be  $Ta_2S_5$ , the analysis being carried out by burning the sulphide in a stream of oxygen, weighing the tantalum oxide left, and estimating the sulphur dioxide produced as barium sulphate.

Tantalum oxide is not appreciably acted on by hydrogen sulphide, even at  $1200^\circ$ .  
T. S. P.

**Formation of Colloidal Gold Solutions by the Auto-oxidation of Aurous Chloride.** LUDWIG VANINO and L. RÖSSLER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 289—290).—When aurous chloride, prepared by heating the auric salt at  $200^\circ$ , is acted on by hot water, a blue colloidal solution of gold is at once obtained. With a large quantity of water, the blue colour is not evident until after about twelve hours; at the same time a gold mirror appears on the surface of the solution. On addition of sodium chloride, the blue colour changes to a reddish tint; potassium hydroxide has no effect on the colour. The production of the colloidal gold is attributed to the change:  $3AuCl = AuCl_3 + 2Au$ .  
H. M. D.

**Preparation of Colloidal Metals by means of Acraldehyde.** NICOLA CASTORO (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 283—289).—Colloidal solutions of gold, platinum, osmium, palladium, ruthenium, iridium, rhodium, and silver are very readily obtained when dilute solutions of salts of these metals are treated with a small quantity of a 33% solution of acraldehyde. The hydrosols obtained in this way are more stable than those formed by reduction with formaldehyde or by the electrical method. The reducing action of the acraldehyde is supposed to be due, not only to the aldehyde group, but also to the double linking. In support of this view it has been found that metallic hydrosols can also be obtained by the action of allyl alcohol. Acid solutions of gold chloride are reduced by allyl alcohol with the production of bright red gold hydrosols. Acraldehyde has no action in acid solutions, and these must first be made neutral or slightly alkaline by addition of potassium carbonate.  
H. M. D.

## Mineralogical Chemistry.

**Samsonite, a Manganiferous Silver Mineral from the Harz.** WERNER and FRAATZ (*Centr. Min.*, 1910, 331—336).—This new mineral was found in the Samson mine at St. Andreasberg, in association with pyrrargyrite, galena, pyrolusite, quartz, calcite,

appearance; they are steel-grey, but red by transmitted light. Analysis gives the formula  $2\text{Ag}_2\text{S}, \text{MnS}, \text{Sb}_2\text{S}_3$ , which is similar to that of pyrrargyrite with part of the silver replaced by manganese.

S.	Ag.	Sb.	Mn.	Cu.	Fe.	$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{SiO}_2$	Pb.	As.	Total.
20.55	45.96	26.33	5.86	0.18	0.22	0.41	0.46	traces			99.86

The associated greyish-black calcite and rose-red apophyllite owe their colour to the presence of some manganese and iron.

L. J. S.

**Action of Acetic Acid on Clays (Kaolin and Allophane).**  
 RUDOLF VAN DER LEEDE (*Centr. Min.*, 1910, 289—295).—Comparative experiments were made with kaolin (anal. I) from Zettlitz, near Carlsbad, Bobemia, and allophane (anal. II) from Ohio. Analysis I corresponds with the ratio  $\text{Al}_2\text{O}_3:\text{SiO}_2=1:2$ , and anal. II with 1:0.756.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	Alkalies	Loss on ignition.	Total.
I.	47.30	41.70	0.20	0.85	0.49	2.06	7.54	100.14
II.	18.47	41.53	0.65	1.62	0.30	0.75	36.85	100.17

These materials were slaken for eight days with 6% or 12% acetic acid. The kaolin was only slightly attacked, about 1—1½% being dissolved and in the solution  $\text{Al}_2\text{O}_3:\text{SiO}_2=1:1$ . Of the allophane, about 1.5% was dissolved, and the ratio of  $\text{Al}_2\text{O}_3:\text{SiO}_2$  in the solution was the same as in the mineral itself. This chemical difference between kaolin and allophane affords a means of distinguishing these two kinds of clay when optical methods fail. Kaolin has resulted by the gradual alteration of felspar, whereas allophane is a colloidal substance precipitated from solution as a jelly (compare Stremme, *Abstr.*, 1908, ii, 1041).

L. J. S.

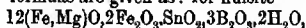
**Synthesis of Anglesite.** GIUSEPPE PIOLTI (*Atti R. Accad. Sci. Torino*, 1910, 45, 373—375).—Immersion of iron pyrites in lead nitrate solution for a period of sixteen and a-half years resulted in the formation on the pyrites of slender needles of anglesite and traces of limonite.

T. H. P.

**Composition of Hulsite and Paigeite.** WALDEMAR T. CHALLER (*Amer. J. Sci.*, 1910, [iv], 29, 543—549).—A re-determination of the boric acid in these supposed new minerals (*Abstr.*, 1908, 507) made by Wherry and Chapin with their new methods (*Abstr.*, 909, ii, 92) gave in analysis II of hulsite previously quoted the figure 10.44 instead of 25.27%; and in analysis III of paigeite, 9.88 instead of 20.89%. The differences are partly accounted for by the presence of tin, which was overlooked in the original analyses. The following new analyses are given: I, of hulsite free from magnetite but containing a considerable amount of insoluble gangue; and II and III, of different samples of paigeite, also containing gangue.

	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$	$\text{SnO}_2$	$\text{B}_2\text{O}_3$	Insol.	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}$	&c.	Total
I.	27.71	4.29	9.11	15.21	7.07	9.20	13.63		[8.78]			100.0
II.	40.32	2.04	4.13	18.67	3.18	9.10	16.10		[5.96]			100.0
III.	35.02	2.12	8.79	14.90	2.80	6.94	18.57	3.10	2.34	[5.432]		100.0

Doubts still exist as to which constituents, especially the calcium, are to be referred to the minerals themselves and which to the gangue. The "probable" formulae are given as: for hulsite



and for paigeite,  $30\text{FeO} \cdot 5\text{Fe}_2\text{O}_3 \cdot \text{SnO}_2 \cdot 6\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , but it is suggested that paigeite may possibly be a mixture of hulsite and an iron borate.

L. J. S.

**Mineral with Optical Scroll Structure Contained in Holocrystalline Phosphorites from Quercy.** ALFRED LACROIX (*Compt. rend.*, 1910, 150, 1388—1390).—Quercy phosphorite contains colophanite,  $\alpha$ -quercyite and  $\beta$ -quercyite, and a holocrystalline type of mineral. The last constitutes fungoid concretions which are found on the walls of cracks in the phosphorite of Mouillac, and also as nodules in clays of the same formation. Its fracture is flinty, of dead white colour, and shows long, interlocked fibres. Under the microscope, it is seen to have the characteristic scroll structure discovered in calcedonite by Michel Lévy, and imitated by Wallerant in organic compounds by melting them in presence of optically active substances. Analysis shows that the mineral is practically identical with dahllite, of which it is supposed to be a special habit.

The author has observed the same helical structure in dufrénite from Rochefort-en-Terre.

R. J. C.

## Physiological Chemistry.

**Acapnia and Shock. VI. Acapnia as a Factor in the Dangers of Anæsthesia.** YANDELL HENDERSON and MARTIN McRAE SCARBROUGH (*Amer. J. Physiol.*, 1910, 26, 260—286).—Anæsthetics prevent shock because they diminish pain-hyperpnea, and thus obviate the development of acapnia. Respiratory excitement during the induction of anæsthesia diminishes the carbon dioxide of the blood, and thus tends to induce subsequent apnœa which may be fatal. Skillful anæsthesia consists in maintaining the threshold of the respiratory centre for carbon dioxide at a nearly normal level, and in avoiding the development either of acapnia or hypercapnia. Under anæsthesia this threshold may be elevated 50% above normal, or depressed 50% below normal. Such a depression causes vigorous hyperpnea, which, if long continued, may result in intense acapnia.

W. D. H.

**Tonometry of the Gases of the Blood.** PIERRE FISKET (*Bull. Acad. roy. Belg.*, 1910, 287—294).—The author has repeated the experiments of Frederiq (*Centr. Physiol.*, 1893, 7; 1894, 8) and of Bohr (*Abstr.*, 1891, 344; 1905, ii, 729), using the apparatus employed

by each of these workers and also the microtonometer devised by Krogh (*Skand. Arch. Physiol.*, 1908, 20, 259). The results obtained show that the tension of the oxygen in the arterial blood of the dog amounts to 13—14% of an atmosphere, that in the alveoli being 18%. For carbon dioxide the tension (3—4% of an atmosphere) is approximately the same as that in the air of the alveoli. The author considers with Fredericq that diffusion alone governs the gaseous exchanges at the surface of the pulmonary alveoli at the moment of hæmatosis, and that consequently Bohr's secretion hypothesis is untenable. Meanwhile, Krogh (this vol., ii, 512), working in Bohr's laboratory, has obtained similar results, thus confirming Fredericq and E. H.

**The Relative Magnitude of the Parts Played by the Proteins and Hydrogen Carbonates in the Maintenance of the Neutrality of Blood.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, 7, 351—358).—The concentrations of hydrogen ions in 8% solutions of the serum-proteins, dissolved in solutions of known acidity or alkalinity, have been determined with the aid of the gas-chain. In passing from the reaction  $0.37 \times 10^{-7} \text{NH}^+$  (the reaction of normal blood) to the reaction  $1.00 \times 10^{-7} \text{NH}^+$  (the reaction seen in marked acid poisoning), 100 c.c. of an 8% solution of the serum-proteins at 34° neutralises the equivalent of 22.5 c.c. of *N*/100-hydrochloric acid. According to L. J. Henderson, the hydrogen carbonates in 100 c.c. of blood in passing through the same range of reactions neutralise the equivalent of 100 c.c. of *N*/100-hydrochloric acid; the proteins are thus about one-fifth as efficient in maintaining the neutrality of normal blood. It cannot be inferred from this that the same holds for tissues and tissue fluids. The proteins of serum are precipitated by alcohol, not in the free form, but as salts. W. D. H.

**The Morphological Detection of Methæmoglobin in the Blood.** G. KRÖNIG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 539—546).—The change of the blood-pigment into methæmoglobin produced by certain poisons (chlorates, etc.) is well-known, and has been detected spectroscopically. The present paper deals with the microscopic changes the corpuscles undergo, and illustrations are given of their disintegration, the separation of pigment from stroma, the clumping of the hæmoglobin, its change into methæmoglobin with accompanying changes in staining reactions, and the ingestion of the red corpuscles in different stages of breakdown, or of the methæmoglobin granules by leucocytes. W. D. H.

**The Capacity of the Animal Body to Produce Multivalent Precipitating Sera.** CASIMIR STRYZOWSKI (*Zeitsch. physiol. Chem.*, 1910, 66, 1—7).—By immunising rabbits against several proteins the anti-serum obtained contains specific precipitins for each. W. D. H.

**Antitypein.** S. COBLINER (*Biochem. Zeitsch.*, 1910, 25, 493—504).—An investigation into the nature of the antitypsin in serum, the

mechanism of its production, and the conditions influencing its variations in quantity. It has no lipid character, but is a true anti-substance. In the human economy whenever excretion from the pancreas occurs, a part of the trypsin is always absorbed again. This acts as a hormone for the cells concerned, and a corresponding liberation of antitrypsin in the blood-stream takes place. G. S. W.

**The Catalase Content of Maternal and Fœtal Blood and the Action of Fœtal Serum on Animals of the Same Species.** GEORG LOCKEMANN and JOHANNES THIES (*Biochem. Zeitsch.*, 1910, 25, 120—150).—The catalase content of rabbit's blood was estimated by measuring the amount of destruction of hydrogen peroxide solution (1%) which takes place when 30 c.c. are left for two hours with 10 c.c. of diluted blood (1:1000) at room temperature. It was found that the blood of the fœtus was poorer in catalase than the maternal blood.

The intravenous injection of small quantities of fœtal blood or serum into pregnant animals causes generally, in the case of rabbits, symptoms of illness, especially when the injection is repeated after several days. The symptoms vary in different cases, and in some cases are manifested in the form of tonic and clonic convulsions, which result finally in the death of the animal. In the case of non-pregnant animals, the first injection is without effect. A second injection after eight days, has an effect as powerful as that on pregnant animals. The results obtained are similar to those found in the phenomenon of anaphylaxis. For this reason, the author suggests that eclampsia may be allied to an anaphylactic action. S. B. S.

**Poisonous Properties of Blood.** J. STUDZINSKI (*Zentr. Physiol.*, 1910, 23, Rprint 8 pp.).—The transfusion of blood from one animal to another of the same species usually provokes a temporary rise of blood pressure, whilst when the second animal is of a different species, a temporary fall of pressure occurs. In some cases, however, these phenomena are reversed. The lowering of pressure is ascribed to the presence of vasodilatin (compare Popielski, Abstr., 1909, ii, 593) in the injected blood. A second injection made after the effects of a previous one have passed off, has no marked action. A solution obtained by adding to defibrinated blood phosphotungstic acid, and removing the excess of this reagent with barium hydroxide, was just as active as the blood itself. This solution when evaporated to one-fourth of its volume and injected into a dog (15 c.c. per kilo. of body-weight) causes the death of the animal, and the heart is found in a condition of extreme diastole. The vasodilatin is soluble in absolute alcohol, and is not precipitated from that solvent by a moderate quantity of ether. The rise of pressure occurring in some cases is said to be due to *vasohypertensin*, solutions of which can be obtained by similar methods. R. V. S.

**Analytical Investigations on Nitrogen and Phosphorus Metabolism and their Relationships.** GEORG GRUND (*Zeitsch. Biol.*, 1910, 54, 173—229).—This simple balance-sheet method of comparing ingesta and egesta cannot settle the question of the

intimate changes which occur in the organs. In the present research on dogs and hens, the organs themselves were investigated, after being freed from blood. In rich protein feeding, the liver takes up more protein, and in hunger loses more than do the kidneys and muscles. The relationship of total phosphorus to total nitrogen in the dog's organs remains fairly constant ( $P_2O_5:N=1:7.1$ ); in the hen, the quotient is constant for the muscles, but in the liver it sinks slightly on protein feeding, and rises greatly on vegetable food rich in phosphorus. The quotient of protein phosphorus to protein nitrogen in the dog's liver on a protein diet sinks to a small degree, and is probably due to changes within the cells. The quotient of residual to total nitrogen shows great variations, and no general rules can be stated. The quotient of protein phosphorus to total phosphorus shows a slight fall in the dog's liver on protein feeding, and runs parallel to the quotient of protein phosphorus to protein nitrogen. W. D. H.

**The Metabolic Influence of Copious Water Drinking with Meals.** C. C. FOWLER and PHILIP B. HAWK (*J. exper. Med.*, 1910, 12, 383—410).—The subject of the experiment, a man aged twenty-two, took 3 litres of water daily with his meals for five days. His weight increased by two pounds, and there was an increase in urinary nitrogen, mainly in the form of urea, ammonia, and creatine; creatinine was diminished, probably because the water stimulates protein catabolism; creatine appeared probably because water causes a partial muscular disintegration; the ammonia increases probably because there is an increased output of gastric juice. The faeces, faecal nitrogen, and faecal bacteria all diminished. The protein constituents of the food were more economically utilised. The result indicates many desirable and no undesirable features. W. D. H.

**The Influence of Fat Subcutaneously Administered on Protein Metabolism.** ERNST HEILNER (*Zeitsch. Biol.*, 1910, 54, 54—63).—Metabolic experiments on rabbits are described, in which the administrations of olive oil by the mouth and subcutaneously are compared. The oil was given in amounts sufficient to satisfy the caloric need of the body; subcutaneous administration did not affect fat metabolism, but raises protein catabolism; the absorption of food so given is very slow, and subcutaneous feeding on fat cannot be recommended for clinical use. W. D. H.

**Nuclein Metabolism in the Pig.** ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1910, 66, 53—62).—Nucleic acid administered to pigs is acted on by nuclease, deamidase, and oxydases; purine bases and uric acid are formed, and a final product is allantoin, which accounts for a small fraction (1—5% only). The purine bases in pig's urine consist mainly of xanthine and hypoxanthine; a small amount of adenine is present, but no guanine. Pöcile found guanine in the urine of a pig suffering from gout, and further investigation of the metabolism in gouty pigs is desirable. W. D. H.

**Effects of Nutrition with Maize. Action of the Gastric Juice on Zein and Gliadin.** II. SILVESTRO BAGLIONI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 512—517).—The author's experiments on the

action of the gastric juice of the dog on zein and gliadin show that the juice has a twofold action on gliadin. In the first phase of the action, the gliadin is degraded into simpler protein products (peptones, gliadoses), the latter being subsequently converted into compounds which are deposited from the liquid as precipitates. The biuret reaction is red during the earlier stages of the reaction, but changes later to violet. As this second action can be prevented by previous heating of the liquid to 92°, it appears to be a true enzymic action. Zein offers considerably more resistance to the action of gastric juice than does gliadin, and it is converted into peptone-like products or zeeses, which are unchanged by further action of the juice.

T. H. P.

**The Nutritive Value of Fish in Comparison with Beef and its Effect on the Urine.** B. SLOWTZOFF (*Zeitsch. physikal. diätet. Therapie*, 1910, 14, 1—20).—Fresh or smoked fish has the same nutritive value as beef, but salted and dried fish is less readily absorbed. As compared with beef, less of the nitrogen leaves the body as urea, and more as residual nitrogen. Urinary indican is increased on a fish diet, but diminished if the fish is cured. Fresh (but not cured) fish increases the absorption of salts in the intestine, and acts favourably on phosphorus and magnesium metabolism; the retention of calcium is smaller on a fish diet.

W. D. H.

**Purine Metabolism. II. The Capacity for Destroying Uric Acid of the Organs of *Scyllium catulus*.** VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1910, 25, 296—300).—The spleen and Wolf's bodies were inactive; kidneys, stomach, intestine, and muscular tissue possess the capacity for destroying uric acid; in the case of the liver, the reaction follows the type of a unimolecular reaction. The reaction is a fermentative process, at any rate in the case of the liver, which is rendered inactive by boiling.

S. B. S.

**Purine Metabolism. III. The Total Nitrogen and Purine Nitrogen in the Organs of *Scyllium catulus*.** VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1910, 25, 411—414).—The author tabulates the results of analyses of the principal organs, those containing the largest amount of purine substances being the pancreas, testicle, and spleen.

S. B. S.

**Purine Metabolism. IV. The Behaviour of the Purine Substances in the Autolysis of the Liver of *Scyllium catulus*.** VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1910, 25, 415—419).—A nucleaso is present in the liver of *Scyllium catulus* which exerts its activity chiefly in the interval between the sixth and twenty-fourth hour of autolysis. The purine bases separated from nucleoproteins by this nuclease are so changed in the process as to lose their character of purine substances. Uric acid could not be detected as a product of the change.

S. B. S.

**The Decomposition of Cellulose in the Horse's Cæcum.** HEINRICH VON HOESSLIN and E. J. LESSER (*Zeitsch. Biol.*, 1910, 54, 47—53).—Scheunert's conclusion is confirmed, that the decomposition

which occurs in cellulose in the cæcum of the horse is due to the activity of micro-organisms. W. D. H.

**Protein Degradation in the Intestine of Man.** ALICE STAUBER (*Biochem. Zeitsch.*, 1910, 25, 187—203).—The method was to observe the hourly output of urea after meals. A constant curve was found for normal individuals after a standard meal; in pathological cases, a deviation from the normal curve was detected. In normal individuals, after washing out the excess nitrogen by drinking large quantities of fluid before the test meal, it was found that the maximum of urea excretion took place between the fourth and fifth hour after the meal; the same fact was observed in several pathological cases. If degraded protein, such as peptones, be substituted for the standard protein of the normal meal, the maximum for the urea output is reached between the first and second hour after the meal. In tuberculous patients, this same maximum was noticed even after a normal meal not containing the degraded proteins. S. B. S.

**The Real Relation of Trypsin to Erepsin.** KARL GLAESSNER and ALICE STAUBER (*Biochem. Zeitsch.*, 1910, 25, 204—218).—Both the small and large intestine contain in the mucous membrane an albumose-splitting enzyme, which is present in the larger quantity in the small intestine. This ereptic action is not due to coli bacilli. Trypsin and the pancreas also contain an ereptic component. The ereptic and tryptic ferment actions can be separated from one another by taking advantage of the fact that blood-serum inhibits only the tryptic action. If the pancreatic duct of a rabbit is ligatured, an increase of erepsin will be found both in the blood and in the small intestine. If the pancreas is destroyed by the injection of paraffin into the gut, erepsin disappears from the intestine. S. B. S.

**The Influence of Sodium Glycocholate on Tryptic Digestion.** G. QUAGLIARIELLO (*Biochem. Zeitsch.*, 1910, 25, 220—238).—The rate of digestion was measured by means of the viscometer. No marked effect on the rate of tryptic digestion could be observed when small quantities of sodium glycocholate were added to the digestion mixture. S. B. S.

**The Influence of Bile Salts on the Pancreatic Digestion of Starch.** GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1910, 25, 239—256).—The viscometer method and estimation of maltose were the chief methods employed. It was found that the amount of sugar formed from starch as a consequence of the action of the pancreatic ferment did not depend on the time and amount of ferment present, being proportional neither to the one nor the other of these changeable factors. The curves therefore representing the rate of reaction are not straight lines, neither have they a simple logarithmic character, being similar in this respect to those representing the tryptic digestion of proteins. Bile salts exert a favourable influence on the rate of digestion, which is independent of the concentration of the ferment and of the time of digest. There is a certain optimum concentration for the favouring



action of bile salts, which is higher than that found normally under physiological conditions of digestion. S. B. S.

**Physiology of Glands. XV. The Relationship between the Physico-chemical Properties of the Gland Proteins and the Secretive Capacity of the Glands.** LEON ASHER and THEODOR KARAULOW (*Biochem. Zeitsch.*, 1910, 25, 305—326).—The glands investigated were the pancreas and kidneys, from which the nucleoproteins were prepared. It was found that the internal friction of alkaline solutions of the nucleoprotein of kidneys was greater than that of those from the pancreas. Addition of electrolytes contained in blood-plasma diminished the viscosity of the solution of kidney nucleoprotein more than it did that of pancreas nucleoprotein. Dextrose showed no marked differential action. The conductivity of solutions of kidney nucleoprotein was greater than that of pancreas nucleoprotein. Addition of electrolytes increased the conductivity of a solution of nucleoproteins in *N*/10-potassium hydroxide more than it did the conductivity of protein-free *N*/10-potassium hydroxide. The effect was more marked in the case of pancreas nucleoprotein solution than in that of kidney nucleoprotein solution.

Measurement of *E.M.F.* in gas chains showed that pancreas nucleoprotein combines with more alkali than does kidney nucleoprotein. The authors explain the results by assuming that a combination of the nucleoprotein with electrolytes takes place, and explain the bearing of their results on Asher's theory, that the granules of the secreting cells act as condensers for substances that are afterwards secreted.

S. B. S.

**The Relationship of Glycogen in the Frog's Ovary to the Time of Year.** KAN KATO. Glycogen in the Frog's Ovary. MAX BLEIBTREU (*Pflüger's Archiv*, 1910, 132, 545—579, 580—599).—The maximum of glycogen in the frog's body occurs in October and November; it sinks during the winter, and a further drop occurs at the spawning season, although even then the body contains a good deal. The liver glycogen follows the same order. The weight of the ovary rises from September to March; the great increase of weight which occurs in April is largely due to water; the glycogen of the ovary is least in the autumn and winter; it rises enormously in the spring, and reaches its maximum at the spawning time, so that more than half of the total glycogen of the body is then contained in the ovary and the eggs.

The second paper fills in some of the details in Kato's work, the results of which are generally confirmed in several species of frog.

W. D. H.

**Oxidations in Living Cells (Sea Urchin).** OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1910, 66, 305—340).—The main estimations made were of oxygen; after fertilisation, the amount used by the egg greatly increases; the addition of phenylurethane to the sea water depresses cell division, but leaves the oxygen consumption almost unchanged. The action of various agents and reagents on

the oxygen consumption was investigated, such as hydrogen ions, hydroxyl ions, various salts and metals, etc. The results are discussed in relation to Loeb's theory of fertilisation and membrane formation, and Overton's theory of narcosis. The importance of intracellular enzymes was not confirmed.

W. D. H.

**Autolysis of Fertilised and Unfertilised Echinoderm Eggs.** ELIAS P. LYON and L. F. SHACKELL (*J. Biol. Chem.*, 1910, 7, 371—378).—*Arbacia* eggs autolysed in chloroform water show an increase of soluble nitrogen in periods varying from days to months; this occurs in acid solutions only. Fertilisation exerts little or no effect. More than one-sixth of the soluble nitrogen is of protein origin; the autolysis of phosphorus is parallel to that of nitrogen. With sperm a similar autolysis occurs, except in acid solutions.

W. D. H.

**The Enzymes which Act on Disaccharides in the Human Embryo and New-born Child. I.** JUSSUF IBRAHIM (*Zeitsch. physiol. Chem.*, 1910, 66, 19—36).—In new-born children, lactase, maltase, and invertase are present in the mucous membrane and contents of the small intestine. In the contents of the large intestine, little or no lactase is found. Invertase appears about the beginning of the fourth month of foetal life, maltase at the end of the same month, and lactase about the eighth month. In the new-born child, invertase and lactase occur in the intestine only; maltase is also present in the blood and pancreas.

W. D. H.

**The Enzymes which Act on Disaccharides in the Human Embryo and New-born Child. II.** JUSSUF IBRAHIM and L. KAUMHEIMER (*Zeitsch. physiol. Chem.*, 1910, 66, 37—52).—Observations by Plimmer's method show that lactase is the last formed of the enzymes which act on disaccharides, and probably is the last digestive enzyme formed in foetal life.

W. D. H.

**The Analysis of Brain, Especially with Regard to the Content in Cholesterol and Fatty Acids.** NIRO MASUDA (*Biochem. Zeitsch.*, 1910, 25, 161—164).—The cholesterol was estimated by Kamagawa and Suto's method, and in addition, the water, solid matter, total nitrogen and phosphorus, higher fatty acids, total ash, and ash insoluble in water were estimated in the cerebrum, mid-brain, and cerebellum from brains of man, ox, horse, and pig. The author tabulates his results.

S. B. S.

**The Constituents of the Tissues which are Concerned in the Wassermann Reaction, Especially Lecithin and Cholesterol.** CARL H. BROWNING, J. CRICKSHANK, and I. MCKENZIE (*Biochem. Zeitsch.*, 1910, 25, 85—87\*).—Fresh ox-liver was extracted with ethyl acetate at 60°. The part that separated on cooling was dissolved in ether and precipitated with acetone, which treatment was repeated twice. The properties of the part soluble in ethyl acetate and those of the other fraction ("pure lecithin") were investigated

\* and *J. Path. Bact.*, 1910, 14, 484—502.

with reference to the following reactions: (a) hæmolytic action, (b) capacity for activating cobra hæmolysis, (c) inhibitory action on the serum complement, and (d) the capacity to act as antigen in the Wassermann reaction. Amongst other results, it was found that alcoholic lecithin solution is capable of dissolving relatively large amounts of cholesterol, and that such a solution is a very efficient substitute for the ordinary tissue extract in Wassermann's reaction.

S. B. S.

Investigations on Smooth Muscle (Dog's Oesophagus). II. Action of Cations. G. FIENGA. III. Replacement of Calcium in So-called Physiological Fluids. GIUSEPPE BUGLIA (*Zeitsch. Biol.*, 1910, 54, 230—248, 249—268).—II. The cations investigated fall into two groups: (1) those which increase muscular tonus—potassium, calcium, strontium, barium, and mercury; (2) those which have the opposite effect—lithium, ammonium, sodium, magnesium, manganese, cobalt, nickel, zinc, and cadmium. There is a difference of intensity in the actions of the various metals, in the reversibility of the action, and in the antagonism of members of the two groups.

III. The replacement of the potassium in Ringer's fluid by various other metals was investigated, but the only one found to give equally good results was cesium.

W. D. H.

The Presence of Iron-containing Lipoids in the Spleen. ROBERT BURROW (*Biochem. Zeitsch.*, 1910, 25, 165—170).—The chief lipid isolated from human spleen was a saturated compound containing 1.37% phosphorus, 0.41% iron, and 1.23% nitrogen (N:P=2:1). In addition, two other iron-containing unsaturated phosphatides were obtained, together with jecorin, lecithin, and cholesterol. The author does not give the methods of preparation.

S. B. S.

Adrenalectomy and Glycosuria. HUGH MCGUIGAN (*Amer. J. Physiol.*, 1910, 26, 287—294).—Removal of the adrenals in rabbits renders the production of salt glycosuria impossible, while phloridzin glycosuria occurs readily. Removal of the adrenals in dogs makes the production of salt glycosuria difficult, but not impossible, and in cats the same operation does not modify the production of salt glycosuria.

W. D. H.

The Cholesterol Ester of the Horny Layer. P. G. UNNA and L. GOLODETZ (*Biochem. Zeitsch.*, 1910, 25, 425—426).—The authors aver that Salkowski's discovery of esters of palmitic acid in specimens from cases of dermatitis exfoliativa is not definitely substantiated, chiefly on the ground that a lanolin ointment might have been employed in the treatment of these cases, and that the palmitic esters were derived from this source.

S. B. S.

The Cholesterol Esters of the Horny Layer. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1910, 25, 427—428).—A reply to Unna and Golodetz (preceding abstract). The author denies the possibility

of the palmitic ester having been derived from lanolin on the ground that the latter on extraction with 93% alcohol never yields snow-white needles melting at 77—78°.

S. B. S.

**The Importance of Iron for Animal Oxidations.** ERNST MASING (*Zeitsch. physiol. Chem.*, 1910, 66, 262—264).—Whether cells and cell nuclei or their nucleoproteins contain iron has been answered differently by former workers. In the present research, cells were selected rich in nuclear material, and from organs (generative organs) where oxidation is vigorous; care was also taken to avoid contamination with hæmoglobin. The sperm of the sea urchin and salmon, and the eggs of the sea urchin, contain the merest traces of iron, in many cases not more than there is in sea-water; it is regarded as doubtful whether iron is really important for oxidative processes.

W. D. H.

**The Influence of Certain Toxins and Antitoxins on the Oxidising and Reducing Capacities of the Tissues.** I. ANDREA PITINI (*Biochem. Zeitsch.*, 1910, 25, 257—261).—The action of diphtheria- and typhus-toxins on the oxidation and reduction processes in rabbits was investigated. The oxidation processes were investigated by Nencki's method, namely, by determining the amount of phenol excreted after the injection of benzene in the animals. The reduction processes were investigated in both the alcoholic and aqueous extracts of the muscular tissue by the method of Helier and Richet. Both typhus- and diphtheria-toxins were found to increase the reduction capacity, and diminish the oxidising capacity of the tissues.

S. B. S.

**Glycolytic Process with Reference to the Work of Stoklasa, Oppenheimer, and Rosenberg.** J. DE MEYER (*Zentr. Physiol.*, 1910, 23, 965—974).—Mainly polemical. The views advanced may be summarised as follows: The glycolytic power of the tissues is not proved to be due to an enzyme secreted by the tissue cells, but is probably the result of the action of an enzyme in the blood on these tissues. The pancreas does not form a glycolytic enzyme, but the favourable action of pancreatic extracts on the glycolysis produced by blood is due to the presence of an amhoceptor or activator in the pancreatic extracts.

W. D. H.

**The Amount of Choline in Animal Tissues.** TOSAKU KIMOSHITA (*Pflüger's Archiv*, 1910, 132, 607—631).—The delicacy of the various tests which have been proposed for choline are compared. For quantitative purposes, Lohmann's method of preparing it from the tissues was employed; it is then weighed as the gold compound, various precautions to prevent loss being described. The intestine, pancreas, spleen, muscle, liver, kidney, and lung all contain choline in amounts varying from 0.01 to 0.03%.

W. D. H.

**Adenase and its Relationship to the Origin of Hypoxanthine in the Organism.** CARL VÖGTLIN and WALTER JONES (*Zeitsch. physiol. Chem.*, 1910, 66, 250—256).—It is pointed out that the

existence of hypoxanthine in a tissue is not a necessary proof of the existence of adenase, an enzyme which converts adenine into hypoxanthine. There are cases, for instance, dog's muscle, where adenase is absent and hypoxanthine present. The importance of the purine enzymes seems to have been exaggerated; at any rate, the following facts point to the existence of other factors as well: 1. The organs of the rat show no purine enzymes; nevertheless rat's urine contains uric acid. 2. The organs of the ape contain such enzymes, but the urine contains little or no uric acid. 3. Ascoli's work on the physiological synthesis of uric acid shows that this may occur when neither a purine ring nor a purine enzyme is present.

W. D. H.

**A New Mode of Formation of  $\beta$ -Hydroxybutyric Acid in the Animal Organism.** HENRY D. DAKIN (*Journ. Amer. Medical Association*, 1910, 54, 1441).—The author finds that acetoacetic acid is reduced to  $\beta$ -hydroxybutyric acid in the animal organism. In experiments in which a quantity of about 10 grams of acetoacetic acid in the form of its sodium salt (8% solution) was injected intravenously into cats and small dogs in the course of four to six hours, the urine secreted during this period was found to contain more than 1 gram of  $\beta$ -hydroxybutyric acid.

$\beta$ -Hydroxybutyric acid and acetoacetic acid are thus mutually interconvertible in the animal organism according to whether oxidation or reduction takes place. Since  $\beta$ -hydroxybutyric acid when present in the urine of diabetics is almost invariably accompanied by acetoacetic acid, it is possible that some part of the former acid may be derived by the reduction of acetoacetic acid.

W. D. H.

**Origin of the Brown Pigment in the Integument of the Larva of *Tenebrio molitor*.** ROSS A. GORTNER (*J. Biol. Chem.*, 1910, 7, 365—370).—The process of coloration in the larva is due to the interaction of an oxydase and a chromogen; it proceeds in the absence of life. It can be inhibited by carbon dioxide and by nitrogen, but proceeds again when oxygen is admitted and the inhibitor removed. The chromogen resembles tyrosine in being not precipitable by phosphotungstic acid. In the pupa stage, the chromogen is absent, but tyrosinase is present both in the pupa and the beetle. A phenolic substance is present in the larva, as also are substances capable of uniting with diazo-compounds to form azo-dyes.

W. D. H.

**Chemistry of Acute Falls in Weight. Relationships between Water and Salts in the Organism.** LUDWIG TOBLER (*Arch. exp. Path. Pharm.*, 1910, 62, 431—463).—Acute loss of body-weight was produced in dogs by the administration of large doses of magnesium sulphate, and death ensues in a few days when the body has lost from 25 to 30% of its weight. The skin and muscles lose most weight, 65% of the total, and half of this is due to loss of water. These parts, however, contain after death 65 to 75% of water, the normal figure being 55%. The different mineral constituents are lost in varying proportions, the greatest loss next to water falling on the chlorine and potassium. Similar conditions obtain after great loss of water by the skin.

W. D. H.

**Biological Differentiation of Milk and Milk Proteins.** FRITZ KOLLMAYER (*Zeitsch. Biol.*, 1910, 54, 64—90).—The capacity to unite with complement renders it possible to differentiate milks biologically; the action is specific, and each protein (caseinogen and the albumin-globulin complex) has its own special action. Milk can by this means be distinguished from serum. In addition to the specific milk proteins, proteins are present in the milk identical with those in the blood, and such proteins are more abundant in colostrum than in fully formed milk. Milk which has been boiled can also be used for the preparation of an anti-serum which reacts with boiled and raw milk. The union with complement of milk antisera, and the action of the antigens does not appear to be dependent on the calcium present. W. D. H.

**Comparative Investigation on the Composition of Caseinogen from Human and Cow's Milk.** EMIL ABDERHALDEN and LEO LANGSTEIN (*Zeitsch. physiol. Chem.*, 1910, 66, 8—12).—So far as total hydrolysis is concerned, the yield of individual amino-acids indicates no difference in the composition of the caseinogen of cow's and human milk. W. D. H.

**Comparison between the Mode of Action of Certain Retarding Salts and the Proteins of Milk Coagulable by Heat on the Coagulation by Rennets of Boiled Milk.** C. GEREER (*Compt. rend.*, 1910, 150, 1357—1360. Compare this vol., ii, 527).—An account of further experiments in support of the theory previously advanced, that those substances which protect fresh milk from coagulation by ferments which act on boiled milk do so by combining with the casein, and are not strictly speaking anti-ferments. Boiled milk containing small quantities of salts of copper, silver, mercury, gold, or metals of the platinum group behaves towards ferments precisely as fresh milk in the absence of these substances. The protective influence of these salts closely resembles that exerted by those proteins of fresh milk which are rendered insoluble by the action of heat. W. O. W.

**Ferments of Milk and their Origin.** JULIUS WOHLGEMUTH and MICHAEL STRICH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 520—524).—It is known that the milk of most animals contains carbohydrate- and fat-splitting ferments, and also an oxydase, reductase, and catalase. A proteoclastic enzyme has so far not been found. The *casease* of Duclaux, which possesses the property of dissolving the casein coagulum formed by rennet, is not normally present in fresh milk, but is the product of the growth of a definite organism. The galactase of Babcock and Russell (compare Abstr., 1900, i, 712) has similar origin. The statement of Spolverini that milk contains pepsin and trypsin, and the researches of Moro are similarly discredited. The authors succeeded in demonstrating the presence of a glycyl-tryptophan-splitting ferment in human milk, and in the milk of the rabbit, cow, goat, and guinea-pig. It was found most abundantly in the first two instances. The ferment is killed in fifteen minutes at 65—70°, but withstands peptic digestion. The rôle of this enzyme in the economy of infantile

nutrition is at present open to question. The possibility of accurate quantitative estimation of diastase in these liquids led the authors to endeavour to discover the origin of these milk ferments by the examination of the diastatic content of the blood, urine, and milk of various animals. Guinea-pigs have more diastase in their blood than dogs, dogs more than rabbits; The diastatic content of the milks of these animals is, however, in the reverse order. From one woman, milk, blood, and urine were obtained. The diastatic contents of these liquids were of the order 200:1:1 during the earlier period of lactation, and at a later period a comparison of milk and blood gave the value of diastatic activity 10:1. Colostrum contains even more diastase than milk during earlier lactation. Cow's and goat's milk contains no diastase, although the blood of these animals has the same diastatic content as that of woman. The conclusion is drawn that the mammary glands of some animals have special capacity for secretion and excretion of blood diastase, although most of the milk diastase, where it occurs, is elaborated in these glands. It is suggested that these glands are the seat of formation of the other enzymes present in milk. That blood diastase can pass into milk was shown by direct experiment. In three instances it was demonstrated that ligaturing the pancreatic duct of a bitch in early lactation produced a great increase of diastase in the blood, urine, and milk. The increase in the blood was much greater than that in milk. The diastatic content of the milk and of the blood returned to normal simultaneously.

G. S. W.

**Accidental Presence of Thiocyanates in Milk and their Origin.** E. D. STÖCKLIN and CROCHETELLE (*Compt. rend.*, 1910, 150, 1530—1531).—Samples of milk showing a rose-red coloration were found to contain thiocyanates. The presence of these substances was traced to the occurrence of mustard oil (from *Cruciferae*) in cattle-cakes on which the cows had been fed.

W. O. W.

**The Fate of the Intermediate Uric Acid in Human Metabolism, and the Allantoin Content of Human Urine; the Recognition and Stability of Allantoin.** WILHELM WIECHOWSKI (*Biochem. Zeitsch.*, 1910, 25, 431—459. Compare Abstr., 1907, ii, 284).—In dogs, nucleic acid given by the mouth is converted, almost quantitatively, into allantoin. Rabbits yield only 40—50% of the nitrogen of nucleic acid in this form. Normal human urine may contain from 5—50% of the ingested purine nitrogen as uric acid. Given subcutaneously, uric acid appears as allantoin for the most part in the case of the dog and rabbit, whilst in the human being about 90% is excreted unaltered, a small fraction not being recovered. The author, disagreeing with Schittenhelm and others, asserts that allantoin, as in other mammals, is produced in the purino metabolism of the human being, but in so small an amount that uric acid must be regarded as the main channel of excretion of purine nitrogen. In the method employed, the urine is put through a lengthy series of precipitation processes in which phosphotungstic acid and mercuric, lead, and silver salts are employed. Finally, the free allantoin is recrystallised from hot water and weighed. A critical examination of the method and its suggested modifications is given.

Pure allantoin undergoes slight decomposition when boiled in solution of distilled water. In a similar manner to uric acid, it yields oxalic acid on shaking with alkali hydroxides. It reduces solutions of certain metallic salts, yields glyoxalic acid on oxidation, and may be used instead of that acid in the Adamkiewicz's reaction. G. S. W.

**Chylous and Pseudo-chylous Ascites.** R. L. MACKENZIE WALLIS and H. A. SCHÖLBERG (*Quar. J. Med.*, 1910, 3, 301—312).—The milky appearance of a pseudo-chylous ascitic fluid is due to a lecithin-globulin complex which is held in suspension by the inorganic salts present; removal of the latter by dialysis precipitates the complex, and the opalescence disappears. The milky appearance is not due to free fat, lipoids, or mucinoid material. W. D. H.

**The Etiology of Beri-Beri.** S. KAJIURA and OTTO ROSENHEIM (*J. Hygiene*, 1910, 10, 49—55).—Beneficial results have been achieved in Japan by merely replacing a certain percentage of rice by other nitrogenous foodstuffs (meat or barley); this is strongly in favour of the view that the disease beri-beri is not produced by a specific poison in rice, but by the unphysiological nature of a rice diet. Rice is poor in calcium and phosphorus; its nitrogen percentage is not markedly lower than that of barley. The beneficial results of barley might therefore be due to the nature of its proteins. The glutadins or alcohol soluble proteins in barley are represented by hordein, and they are absent in rice, and, possibly, this absence will explain the non-efficiency of a rice diet. On this hypothesis, experiments on fowls were undertaken with white or peeled rice from Japan. A simple diet of this rice causes in these birds a fatal disease identical with, or very similar to, beri-beri, independently of influences of climate or locality; the addition of hordein in the quantities used, or of large quantities of calcium carbonate or phosphate, did not, however, prevent the disease. W. D. H.

**Biochemistry of Growth. I. The Total Nitrogen Metabolism of Rats Bearing Malignant New Growths. II. Distribution of Nitrogenous Substances in Tumour and Somatic Tissues.** WILHELM CRAMER and HAROLD PRINGLE (*Proc. Roy. Soc.*, 1910, B, 82, 307—315, 315—320).—Less nitrogen is necessary to build up tumour tissue than the same weight of somatic tissue. Animals with tumours maintain a positive nitrogen balance, and the nitrogen retention increases with the size of the tumour. The tumour cells have no special affinity for nutritive material, nor do they proliferate at the expense of the other tissues; their nitrogenous material is derived from a sparing action on protein metabolism. No evidence of a toxin was found. Weight for weight cancer cells contain only about three-quarters of the protein in ordinary tissue cells, so that a large mass of tumour is built from a comparatively small weight of protein food; the abietic products, however, are slightly more abundant in cancer than in normal cells. Fetal tissues and probably other rapidly growing tissues have also a relatively low nitrogen percentage. W. D. H.



**Peptolytic Enzymes in Cancer and other Tumours.** III. EMIL ABDERHALDEN and FLORENTIN MEDIGRECHANU. IV. F. ABDERHALDEN and LUDWIG PINCUSCHN (*Zeitsch. physiol. Chem.*, 1910, 68, 265—276, 277—283).—III. The various tumours of rats and mice investigated always contain peptolytic enzymes, but with one exception no difference between those and those of normal liver cells were noted. In some cases, the tissue juice of ulcerated tumours acted more vigorously than that of non-ulcerated tumours. The exception just alluded to is that the juice of all the mouse tumours and most of those from rats produces cleavage of silk-peptone, whereas that of normal tissue does not. The serum of normal rats cleaves glycyl-L-tyrosine and *dl*-leucyl-glycine; that of mice cleaves the first-named dipeptide; the second was not investigated. It is probable that the serum of dogs (which normally contains no peptolytic enzymes) with tumours contains such enzymes.

IV. The difference just noted in animal tumours holds also for those in man, and may be of diagnostic value. W. D. H.

**Effect of Electric Bath Treatment of the Insane on the Urinary Creatinine.** R. L. MACKENZIE WALLIS and EDWIN GOODALL (*J. Mental Sci.*, April, 1910).—The excretion of creatinine in the insane is usually low; it is not influenced by ordinary warm baths, but electric baths using the sinusoidal current slightly increase it, possibly by the effect on the muscles. W. D. H.

**Choline in Pathological Cerebro-spinal Fluid.** MAX KAUFFMANN (*Zeitsch. physiol. Chem.*, 1910, 68, 343—344).—The present tests for choline are not regarded as satisfactory, but the base which has been described as such in normal and pathological cerebro-spinal fluid is "certainly not choline." What it is is left uncertain, as the author had the misfortune to lose the greater part of the substance he had collected from six and a-half litres of fluid.

W. D. H.

**The Non-coagulable Nitrogen of Sera of Normal, Syphylitic, and Tumour Cases.** M. TAKEMURA (*Biochem. Zeitsch.*, 1910, 25, 505—507).—An investigation of the "non-coagulable nitrogen" of certain normal and pathological sera before and after autolysis at 55°. The "total nitrogen" of serum from patients with tumours is not greater than in normal cases. Before autolysis, there is more coagulable nitrogen than the normal in carcinoma cases. After autolysis, the sera of carcinoma cases again gave higher "non-coagulable nitrogen" values than the normal and sarcoma cases; in three syphylitic cases having a positive Wassermann reaction, the sera had normal values; in three cases of paralysis were found still more non-coagulable nitrogen than in the cancerous patients.

G. S. W.

**Phosphorus-content of Sera in Normal, Syphylitic, and Carcinoma Cases.** M. TAKEMURA (*Biochem. Zeitsch.*, 1910, 25, 508—509).—Small differences were observed between the values for the total phosphorus-content of the sera examined. Those giving a

positive Wassermann's reaction for syphilis contained more phosphorus than normal. The sera of carcinoma patients gave similar results.

G. S. W.

#### Behaviour of Elementary Sulphur in the Animal Organism.

ARTUR KONSCHIEGG (*Arch. exp. Path. Pharm.*, 1910, 62, 502—517).—Administration of sulphur to dogs produces a rise in the total sulphates and the "neutral sulphur" of the urine, as previous observers have stated. There is also a marked increase in the ethereal sulphates, due almost exclusively to increase in the phenolsulphuric acid; the indoxyl sulphate hardly alters at all. The urinary nitrogen is unaltered. The drug almost always produces diarrhoea, and the sulphates of the faeces are increased.

W. D. H.

The Formation of Ethereal Sulphates from Thiocarbamide. NIRO MASUDA (*Zeitsch. physiol. Chem.*, 1910, 67, 28—34).—Thiocarbamide given subcutaneously in rabbits increases the "neutral sulphur" of the urine markedly; it is also in part found as such, and part as ethereal sulphate. Increase in the latter is therefore not primarily due to administration of phenol, as some have supposed.

W. D. H.

The Composition of Blood, Urinary Excretion, and Lymph Formation after the Intravenous Injection of Solutions of Colloids alone and in Conjunction with Crystalloids. ANGELO PUGLIESE (*Zeitsch. Biol.*, 1910, 54, 100—152).—The diuretic action of hypertonic solutions of sodium chloride shows very small changes whether the salt is injected into the blood alone or in combination with gelatin and gum arabic, but the excretion of the salt occupies a longer time. The solids of the blood undergo a diminution if the salt solution is hypertonic or hypotonic and mixed with the colloid; in the former case, the osmotic pressure is raised, and in the latter it falls: this outlasts the diuretic effect. If the salt alone is injected, the blood is at first diluted, but soon it becomes more concentrated. The crystalloid and colloid mixture also causes a great increase in the lymph flow, and the osmotic pressure and chloride concentration of the lymph are raised.

W. D. H.

Decomposition of Chloroform in the Organism. MAURICE NICLOUX (*Compt. rend.*, 1910, 150, 1260—1263).—From experiments on dogs, in which the animals were placed in a globe and treated with air containing a known proportion of chloroform vapour, the total amount of chloroform eliminated also being determined, the author arrives at the conclusion that during anaesthesia and the period of recovery about 50% of the chloroform fixed by the blood and tissues undergoes decomposition. Experiments in which anaesthesia was effected by ingestion of chloroform water led to the same result.

W. O. W.

The Behaviour of Furylpropionic Acid in the Animal Body. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1910, 25, 272—283).—After

administration of furylpropionic acid to a dog, furylacrylyluric acid was the main product recovered in the urine, the quantity obtained being equivalent to 21.5% of the furylpropionic acid administered. About 18.5% was recovered as pyromycuric acid, so that about 40% of the furylpropionic acid administered escaped destruction. The author gives synthetical methods for preparing the various substances in question. Pyromycuric acid (m. p. 165°) was obtained by the action of pyromucyl chloride on glycine. Furylacrylyluric acid (m. p. 218—219°) was obtained by the action of furylacryl chloride (m. p. 34°) on glycolic acid, and furylpropionyluric acid (m. p. 118°) by the reduction by sodium amalgam of furylacrylyluric acid.

S. B. S.

**Pharmacological Action of Harmaline.** JAMES A. GUNN (*Trans. Roy. Soc. Edin.*, 1910, 47, II, 245—272).—Harmaline resembles quinine in being relatively much more toxic to mammals than to frogs. In the cases of the guinea-pig, rabbit, and cat, doses exceeding about 0.1 gram per kilogram were fatal, whilst for frogs the minimum lethal dose is 0.25 gram per kilogram. The pharmacological action of the substance also resembles quinine, in that it is of a non-selective type; it affects specialised tissues, such as voluntary muscle and the muscle of the heart, blood vessels, and uterus, and the cells of the central nervous system, whilst its action on less highly differentiated cells (protozoa, ciliated epithelium) has already been observed. In frogs, lethal doses rapidly produce paralysis of respiration, and in mammals, arrest of respiration due to paralysis of the respiratory centre is the chief cause of death from harmaline poisoning.

R. V. S.

**The Behaviour of Mono-palmityl-L-tyrosine, Distearyl-L-tyrosine, and p-Aminotyrosine in the Organism of an Alcaptonuric Person.** EMIL ANDERHALDEN and RUDOLF MASSINI (*Zeitsch. physiol. Chem.*, 1910, 66, 140—144).—The question whether the compounds of fatty acids and aromatic amino-acids can be broken up by the body cells was investigated by giving them to an alcaptonuric patient; in spite of a deleterious effect which they exert on metabolism, the question is answered in the affirmative, for the homogentisic acid which originates from tyrosine was increased in the urine.

A similar result as judged by an increase in the reducing power of the urine followed the administration of p-aminotyrosine.

W. D. H.

**Pharmacological Properties of Picric Acid.** FRANCESCO MOTOLESE (*Arch. Farm. speriment.*, 1910, 9, Reprint, 47 pp.).—With both leucocytes and infusoria, picric acid in the concentration 1:2000 coagulates the protein matter, and thus exerts an immediate fixing action. At the concentration 1:10,000, the acid does not injure the vitality of the infusoria, on which it exerts a marked negative chemotactic action; with the leucocytes, the vital manifestations are depressed and death ultimately caused, owing to the solution of the protoplasm, the same action being produced, although more slowly, at

the concentration 1 : 20,000. In the proportion 1 in 30,000, the acid is inactive towards the leucocytes. Picric acid has an astringent action superior to that of zinc sulphate, alum, or lead acetate, and almost equal to that of basic lead acetate. The acid is possessed of considerable diffusivity, owing to the fact that it is an electrolyte. The permeability of the cornea to picric acid is very slight, and less than that of the conjunctiva.

T. H. P.

**Pharmacological Action of Protocatechyltropine.** CHARLES R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1910, 47, II, 273—285. Compare Jowett and Hann, *Trans.*, 1906, 89, 364).—From experiments on anaesthetised rabbits and cats, and on frogs, the author finds that protocatechyltropine when subcutaneously administered paralyses the vagal endings in the heart, but is much less powerful than atropine or even homatropine. In certain doses, it paralyses the respiration temporarily; this action is due to paralysis of the respiratory centre, and not to a peripheral action. A gradual fall of blood pressure usually occurs, but this does not seem to be connected with the action on the respiration. In cats, a rise of blood pressure is sometimes observed, owing to the paralysis of the vagal endings. It was not found possible to show any separate pharmacological actions of the two groupings in the compounds.

R. V. S.

**The Behaviour of Phloridzin after Extirpation of the Kidneys.** KARL GLAESSNER and ERNST P. PICK (*Pflüger's Archiv* 1910, 133, 82—86).—Polemical against Leschke (this vol., ii, 530). The authors consider that his work, so far from contradicting, confirms their own.

W. D. H.

**Strophanthus sarmentosus; its Pharmacological Action and its Use as an Arrow Poison.** SIR THOMAS R. FRASER and ALISTER T. MACKENZIE (*Trans. Roy. Soc. Edin.*, 1910, 47, II, 341—410).—The alcoholic extract of the mature seeds of this plant contain a substance having the properties of a glucoside. On adding concentrated sulphuric acid to the dry extract, a brown colour, becoming violet, is developed. The pharmacological action of the extract is very similar to that of *S. hispidus* (compare Abstr., 1890, 262), the chief features of its action being the effects on the heart and skeletal muscles. Certain arrow poisons used in Nigeria, and said to be prepared from this plant, were found to behave physiologically in the same way as the alcoholic extract, so that in all probability they are obtained from that source.

R. V. S.

**Pharmacological Action of Tutu, the Toot Plant of New Zealand.** CHARLES R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1910, 47, II, 287—316).—The author has arrived at conclusions in agreement with those of Fitchett and Malcolm (Abstr., 1909, ii, 919) in respect of the experiments common to both investigations. The epileptiform convulsions caused by tutin are mainly of cortical and pontine origin, and the convulsions arising in the pons are very susceptible to anaesthetics. In rabbits, all doses which produce an

obvious action cause a fall of body temperature. When heated on the water-bath for three hours with a 1% solution of hydrochloric acid, or when raised to boiling temperature with 1% sodium hydroxide or 0.05% calcium hydroxide, tutin is decomposed, and the decomposition products have no physiological action. Coriamyrtin, which is obtained from another species of *Coriaria* (*C. myrtifolia*), is a more powerful convulsant than tutin, and it is more rapid and transient in its action.

R. V. S.

Influence of Dietary Conditions on Physiological Resistance. NELLIS B. FOSTER (*J. Biol. Chem.*, 1910, 7, 379—419).—Some dogs were fed liberally, others scantily, on protein in order to test their relative resistance towards abrin and ricin poisoning. The total number of experiments is too small to exclude other factors, such as breed, idiosyncrasy, etc., for whether they succumbed or survived was not related at all to their diet.

W. D. H.

The Toxicity of Atoxyl. K. MUTO (*Arch. exp. Path. Pharm.*, 1910, 62, 494—501).—The lethal dose for a mouse weighing 10 grams is 0.003—0.005 gram; for a frog weighing 15 grams, about 0.005, and for rabbits about 0.2—0.3 gram per kilo. of body-weight. In dogs the most marked post-mortem signs are congestion and hæmorrhages in kidney, intestine, and heart. Estimations of the amount of the drug which passes into the urine in rabbits are given.

W. D. H.

Biochemical and Therapeutical Studies on Trypanosomiasis. ANTON BREINL and MAXIMILIAN NIERENSTEIN (*Ann. Trop. Med. and Parasit.*, 1909, 3, 395—420).—The following conclusions were drawn as to the action of atoxyl: (a) after injection, a comparatively small amount combines through the amino-group with serum proteins and forms "atoxyl-serum"; the greater part is secreted in the urine partly unchanged as *p*-aminophenylarsinic acid, partly oxidised in the form of *p*-hydroxyphenylarsinic acid and as hydroxycarbaminophenylarsinic acid, and partly as free inorganic arsenic; (b) from atoxyl-serum, arsenic is set free through an oxidation process caused by the oxidative ferments present, and probably also by trypanosomes, whereby the aromatic nucleus is destroyed; (c) at the same time reduction takes place in the intestines, whereby atoxyl is reduced to aniline and arsonious acid; (d) the arsenic which is formed by oxidation acts in the nascent state on the trypanosomes.

The authors have investigated the trypanocidal action of a large number of other arsenic compounds and dyes on various animals, but without finding any with distinctly marked action. The substances investigated include acetylated atoxyl, salicyl-atoxyl, formyl-atoxyl, sodium-*p*-hydroxyphenylarsinate, disodium azobenzene-4-arsinate, tetra-sodium phenazine-4-arsinate, sodium di-*p*-aminophenylarsinate, sodium 4-acetyl-amino-3-methylphenylarsinate, and various derivatives of the same, and certain antimony compounds.

The authors give a résumé of various investigations on the resistance to atoxyl acquired by trypanosomes, and conclude that the immunity is often acquired against the "atoxyl-serum," and the resistance only holds good in the animal in which it is acquired.

They also give results of experiments on the time required for destruction of the trypanosomes in the bodies of various animals, and on the value of sub-inoculations. S. B. S.

**The Physiological Action of Cyanamide and Some of its Derivatives.** ALBERT STUTZER and JULIUS SÖLL (*Biochem. Zeitsch.*, 1910, 25, 215—219).—The toxic dose of cyanamide for guinea-pigs was 0.4 gram per kilo. of weight. Dicyanamide given *per os* to a dog in doses of 5 grams per kilo. of weight, administered over five days, produced no toxic effect; toxic effects were observed, however, on guinea-pigs with smaller doses. The hydrochloride of guanylearbamide was also non-toxic to dogs in relatively large doses, but produced toxic effects on guinea-pigs in smaller doses. Diguandine hydrochloride, guanylearbamidesulphonic acid, and guanidylacetic acid were found to be non-toxic. S. B. S.

**Toxolecithides.** JULIUS MORGENROTH and R. KAYA (*Biochem. Zeitsch.*, 1910, 25, 88—119).—The experiments tend to show that the hæmolytic action of cobra-poison is of two-fold nature, and can be activated either by a serum complement like an ordinary amboceptor or by means of lecithin. The following facts support this hypothesis: hæmolysis in presence of serum takes place only at higher temperatures, whereas that in presence of lecithin takes place at 0°; if the cobra poison is heated to 80°, it almost loses its capacity of being rendered hæmolytic by the addition of the serum complement, whereas the property of being rendered hæmolytic by lecithin remains, although weakened; on treatment with acids or alkalis, the amboceptor-like property is destroyed, whereas the power of being rendered hæmolytic by lecithin remains intact after treatment with acids, and is destroyed to a small degree after treatment with alkalis. On allowing the cobra poison to remain with complement before adding the blood-corpuscles, the former is destroyed and no hæmolysis takes place. The complement-destroying property of the poison can be inhibited by a specific anti-toxin, such as Calmette's serum, which also inhibits the amboceptor-like function as regards hæmolysis. The amboceptor-like action of the poison is not typical, in that the supposed amboceptor cannot be bound by the blood-corpuscles, even in the presence of the complement; neither could any binding of the lecithide with blood-corpuscles be demonstrated. S. B. S.

## Chemistry of Vegetable Physiology and Agriculture.

**Does Water Sterilised by Ultra-violet Light contain Hydrogen Peroxide? Sterilising Power of Hydrogen Peroxide.** JULES COURMONT, TH. NOGIER, and A. ROCHAIX (*Compt. rend.*, 1910, 150, 1453—1454. Compare Abstr., 1909, ii, 753).—The length

of time required to produce appreciable amounts of hydrogen peroxide when a quartz-mercury lamp is immersed in water renders it unlikely that the sterilising action of ultra-violet light is due to the formation of this substance. The authors were unable to detect hydrogen peroxide in water which had been in contact with the lamp for twenty minutes. Water containing *Bacillus coli*, which was sterilisable by ultra-violet light in a few seconds, required to be treated with 1.188 grams of hydrogen peroxide per litre for three hours in order to become sterile.

W. O. W.

The Kinetics of the Killing of Bacteria in Oxygen of Varying Concentrations and at Different Temperatures. THEODOR PAUL, GUSTAV BIRSTEIN, and ANTON REUSS (*Biochem. Zeitsch.*, 1910, 25, 367—400).—The rate of death (disinfection rate) of dried bacteria (staphylococci) in oxygen-nitrogen mixture follows the equation of a unimolecular reaction, by means of which the constant for the rate of disinfection can be calculated. This constant is approximately proportional to the square-root of the oxygen concentration. The rate of death of staphylococci follows the same law as the slow oxidation of phosphorus. The temperature-coefficient of the disinfection rate is not constant, but increases with increasing temperature between 18° and 37°. The deviation of disinfection processes from Henry's law is attributable to the dissociation equilibrium of oxygen:  $O_2 \rightleftharpoons 2O$ . Adsorption isotherms can also be employed to explain the deviation. The decrease of the temperature-coefficient of the disinfection rate also suggests the action of adsorption processes. The "garnet method" of Krönig and Paul for studying disinfection phenomena (*Zeitsch. Hyg. Infectk.*, 1897, 25, 1) has proved itself of value in this research.

S. B. S.

Variability of the Proteolytic Power of the Anthrax Bacillus. JEAN BIELECKI (*Compt. rend.*, 1910, 150, 1548—1550).—Successive cultures of anthrax bacillus taken from the same colony show gradually decreasing proteolytic activity, probably through inhibitory action of the peptone in the medium. In a medium containing no peptone, the proteolytic power shows little change with successive cultures, but increases if these are carried out alternately with peptone-containing and peptone-free solutions. The products of autolysis appear to stimulate diastatic activity, but new generations of the bacillus destroy the enzyme formed by the older ones.

W. O. W.

Determination of Volatile Acids in Fermentation Products of Certain Microbes by Duclaux's Method. G. SELIBER (*Compt. rend.*, 1910, 150, 1267—1270).—With certain reservations the amount of volatile acids formed during putrefactive decomposition by bacteria is a characteristic of the particular bacillus present; especially is this the case with *B. butyricus*. Results in many cases, however, depend on the character of the medium; thus, to obtain constant values for *B. butyricus*, calcium carbonate must always be present.

W. O. W.

**Emulsion Lævulan, the Product of the Action of Visco-saccharase on Sucrose.** MAATINUS BEYERINCK [and D. C. J. MINCKMAN] (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 12, 795—798. Compare this vol., i, 450).—Solutions of sucrose in tap water containing traces of potassium nitrate and phosphate inoculated with *B. mesentericus* (the common hay bacterium) change into a milk-white emulsion, and a thick, transparent slime layer is slowly formed at the bottom of the flasks. The lævulan formed is best precipitated with 50% alcohol, and, after dissolving in boiling water and again precipitating, is obtained as a colourless, nearly tasteless powder. This lævulan has  $[\alpha]_D - 80^\circ$  approximately; it is very strongly opalescent in solution, does not reduce Fehling's solution, and is not attached by alcoholic and lactic acid ferments, although decomposed by butyric acid ferments. Hydrolysis with boiling acids converts it into lævulose, the product having  $[\alpha]_D - 70^\circ$ , or, after prolonged heating,  $-64^\circ$ , which indicates partial destruction of the lævulose.

Hay bacteria produce no dextran at all; their cell wall consisting of lævulan. Other bacteria produce dextran,  $[\alpha]_D + 132^\circ$ , alone from sucrose. The slimy cell-wall substances produced by various micro-organisms from dextrose, lævulose, and maltose are of a different nature from lævulan and dextran.

It is considered proved that lævulan and similar cell-wall substances are produced in consequence of the action of enzymes. E. F. A.

**Influence of Concentration of Sucrose on the Paralysing Action of Certain Acids on Alcoholic Fermentation.** M. ROSENBLATT and Mme. M. ROSENBLATT (*Compt. rend.*, 1910, 150, 1363—1366. Compare *Ahstr.*, 1909, ii, 752).—The presence of sucrose diminishes the inhibitory effect of acids on fermentation, its efficiency in this respect increasing with concentration up to 12.5% of sucrose. The protective effect is most marked at those minimum concentrations of acid which in the absence of sucrose completely inhibit fermentation. In the case of acetic acid, for example, four times as much is required to inhibit fermentation in the presence of 10% of sucrose as when only 1.25% of this substance is present.

W. O. W.

**Alcoholic Ferment of Yeast-Juice. V. Function of Phosphates in Alcoholic Fermentation.** ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1910, B, 82, 321—330. Compare this vol., i, 292).—Addition of dextrose or lævulose to yeast-juice in presence of excess of phosphate results in a period of accelerated fermentation; 1 mol. of carbon dioxide is evolved for each mol. of sugar added.

When the available phosphate present is greatly reduced, the total fermentation is very small. Addition of small amounts of phosphate produces a relatively large increase in the total fermentation.

A hexosephosphate when digested with yeast-juice is hydrolysed by an enzyme, hexosephosphatase, with production of free phosphate and a sugar capable of being fermented by yeast.

In the chemical changes which the mol. of sugar may undergo in fermentation, 2 mols. of sugar are involved.

N. H. J. M.



**Influence of Nutrition on the Diastase Formation of Yeast.** K. SAITO (*Woch. Brauerei*, 1910, 27, 181—183).—The tabulated results of experiments on the formation of diastase in cultures of *Aspergillus oryzae* under varying conditions of nutrition. As sources of nitrogen, peptone, tyrosine, leucine, alanine, asparagine, glycine, carbamide, ammonium tartrate, or ammonium oxalate were employed; whilst the carbohydrates were supplied by dextrose, levulose, galactose, sucrose, maltose, lactose, and glycerol. In a second series of experiments the same sugars were employed in conjunction with inorganic nitrogen, such as ammonium salts of inorganic acids, potassium nitrate, or calcium nitrate.  
F. M. G. M.

**Protein Formation in Ripening Seeds.** ERNST SCHULZE and ERNST WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1910, 65, 431—476).—During the ripening of leguminous seeds, the percentage of proteins increases considerably, whilst the non-protein nitrogen diminishes. In the case of *Phaseolus vulgaris*, no absolute decrease of non-protein nitrogen was observed. Peas, however, showed a loss of non-protein nitrogen during ripening, although not great enough to account for the increase of proteins.

It is shown that the hulls of peas contain, in addition to considerable amounts of asparagine, small quantities of arginine, histidine, tryptophan, monamino-fatty acids, choline, and trigonelline, and that the same substances occur in the hulls of *Phaseolus vulgaris*. The non-protein nitrogenous compounds of the hulls are, therefore, very similar to those supplied to leguminous seedlings from the cotyledons.

Unlike the hulls, unripe pea seeds contain very little asparagine; they contain glutamine, which has not yet been detected in the hulls. It is suggested that asparagine migrates from the hulls to the seeds, where it is rapidly utilised for the production of proteins; that glutamine may also be present in the hulls, and that it passes into the seeds and accumulates there.

Milk-ripe wheat seeds contain only very small amounts of non-protein nitrogen. Monamino-fatty acids were found, and arginine seems to be present. No asparagine was found.

Attempts to detect in unripe seeds of peas and beans an enzyme which produces ammonia from asparagine were unsuccessful.  
N. H. J. M.

**Action of Some Hydrolysable Salts on the Higher Plants.** ACH. GRÉGOIRE (*Bull. Soc. chim. Belg.*, 1910, 24, 200—209).—Rye plants were grown in cylinders containing nutrient salt solution, to each of which had been added a hydrolysable salt, formed from a strong base and a feeble acid. Those selected were calcium silico-humate, calcium carbonate, sodium-zeolite (analcime), and calcium zeolite (heulandite). Calcium silico-humate is unfavourable to the development of the rye plant; calcium carbonate slightly retards growth. Analcime causes six times as much growth as in its absence, and heulandite favours 59% more growth. The same relation is found in the amount of mineral matter taken up by the plants under the conditions.

Rye has a great affinity for silicic acid, and the plants were found to have taken up a considerable quantity; in the case of the control solution and that containing calcium carbonate, this silica can only have been derived from the glass vessel. The zeolites cause a very considerable increase in the amount of silica in the plant, but this is not considered to have any influence on their action in facilitating growth.

In brief, the experiments indicate that hydrolysable salts, although themselves lacking any value as nutritive elements, have a specific influence on plant growth: this influence may be positive or negative according to the salt.

E. F. A.

**Assimilation of Free Atmospheric Nitrogen by Plants.** EVA MAMELI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 501—504).—The authors have cultivated a number of different cryptogams, phanerogams, and aquatic plants in closed vessels under sterile conditions, nutriment being supplied in the form of solutions free from nitrogen compounds. The results show that the assimilation of free nitrogen from the air is a general phenomenon with plants, which, however, vary considerably in their capacity for such assimilation.

T. H. P.

**Hairs of *Stellaria Media* and the Assimilation of Nitrogen by Plants.** THOMAS JAMIESON (*Ber. deut. bot. Ges.*, 1910, 28, 81—83).—A reply to Kny (this vol., ii, 443). Fairly large amounts of protein were detected in the club hairs by three usual methods, not described (compare Zemplen and Roth, *Erdészeti Kísérletek, Selmezbánya*, 1898, Heft 1—2; Jamieson, *Rep. Agric. Research Assoc.*, 1907—8).

N. H. J. M.

**Do Malt Infusions Contain Antidiastase?** ALBERT J. J. VANDELDE (*Bull. Soc. chim. Belg.*, 1910, 24, 198—200).—A filtered infusion of green malt was divided into three parts, which were untreated, heated for thirty minutes at 55°, and heated for thirty minutes at 65° respectively. Tested by Lintner's method, the infusion heated at 55° had a slightly greater diastatic activity than the untreated infusion, but that heated at 65° was far less active. These facts are interpreted as indicating the presence of a small quantity of antidiastase approximately equal to the labile enzyme present.

E. F. A.

**Vernin (A Guanine Pentoside Occurring in Certain Plants).** ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1910, 66, 128—136).—This name is given to a nitrogenous substance isolated from young green plants of *Vicia sativa*, *Lupinus albus*, and *Trifolium pratense*, etiolated seedlings of *Cucurbita Pepo*, ripe seeds of *Lupinus luteus*, and *Arachis hypogaea*, unripe seeds of *Pisum sativum*, pollen of *Corylus avellana* and *Pinus sylvestris*, also in ergot. It occurs only in small quantity, and cannot always be detected, being apparently used up at some period subsequent to its formation. It is most conveniently prepared from etiolated seedlings of *Cucurbita Pepo* two and a-half to three weeks old.

The author assigns the formula  $C_{10}H_{18}O_5N_6$ . On hydrolysis with dilute sulphuric acid, vernalin yields guanine and a pentose, which could not be identified because the initial quantity of material was so small, but was shown to be levorotatory. Vernalin is therefore a guanine pentoside. Its solubility in water is only 1 part in about 1320 at 17–18°, but it is more soluble in hot water. On cooling, it is deposited as fine needles or flat prisms,  $C_{10}H_{18}O_5N_6 \cdot 2H_2O$ . A solution in *N*/10-sodium hydroxide was strongly levorotatory; for a 2% solution,  $[\alpha]_D$  at 20° = –60°; solutions in dilute sulphuric acid gave little or no rotation.

It is insoluble in absolute alcohol. Its aqueous solution is precipitated by phosphotungstic acid in presence of hydrochloric or sulphuric acids. Silver nitrate gives a transparent, yellow precipitate soluble in ammonia. Mercuric nitrate also gives a precipitate. Picric acid slowly throws down a picrate in aggregates of small crystals, brush-like or star-shaped under the microscope, melting at about 190°.

E. J. R.

**Migration of Alkaloids in Grafts of Solanaceae on Solanaceae.** MAURICE JAVILLIER (*Compt. rend.*, 1910, 150, 1360–1363).—A number of cases of grafting have been examined in order to ascertain the extent to which migration of alkaloids takes place between the subject plant and the grafted portion. Negative results were obtained with grafts of *Belladonna* or tobacco on the potato plant, and with tobacco on tomato. A mixed graft of *Belladonna* on tomato gave physiological indications of migration, whilst in the inverse case more distinct evidence, both chemical and physiological, was obtained for the migration of mydriatic alkaloids.

W. O. W.

**Presence of Boron in Tunisian Wines.** BERTAINCHAND and GAUVRY (*Ann. Chim. anal.*, 1910, 15, 179–180).—The wines grown in the provinces of Bir-Kassa and Potinville (Tunis) were found to contain traces of boron as a natural constituent.

L. DE K.

**Presence of Tartaric Residues from Wine in an Antique Vase.** GEORGES DENIGÈS (*Compt. rend.*, 1910, 150, 1330–1331).—A vase dating from the first century A.D., discovered at Bordeaux, contained some coloured crystalline grains in which potassium hydrogen tartrate has been identified.

W. O. W.

**Composition of Milk Yielded by Cows Fed on Pasture Manured with Phosphates and Potash.** JOHN GOLDING and SYDNEY G. PAINE (*Analyst*, 1910, 35, 246–247).—Experiments showing that the use of superphosphate and potassium sulphate on a plot of poor soil used for pasturage, although increasing the quantity of milk yielded by the cows, had practically no effect on the non-fat solids of the milk, not even on the mineral constituents thereof. The fat, however, showed a decided decrease.

L. DE K.

**Soil Solution.** FRANK K. CAMERON (*J. Physical Chem.*, 1910, 14, 393–451).—The following subjects are discussed: (1) Absorption

by soils, including imbibition, the formation of solid solutions in the soil, and adsorption. (2) The relation of plant growth to concentration. (3) The balance between supply and removal of mineral plant nutrients. (4) The organic constituents of the soil solution, in which it is shown that the presence of organic dissolved substances in the nutrient medium produces effects on a growing plant of as great or even greater magnitude than those produced by inorganic dissolved substances. (5) Fertilisers. (6) Alkali, that is, the accumulation of soluble mineral substances at or near the surface of the soil under exceptional conditions of prolonged draught, a phenomenon which is pronounced in arid and semi-arid regions.

T. S. P.

**Fertilising Value of Rain Water.** JOHANNES C. BRÜNNICH (*Ann. Rep. Dept. Agric. and Stock, Queensland, 1908-9*, 59-60. Compare von Feilitzen and Lugner, this vol., ii, 444).—Analyses of twenty samples of rain water collected at (1) Brisbane observatory; nineteen from (2) Bungeworgorai, Roma, and twelve from (3) Kamerunga, Cairns, North Queensland. The average amounts of nitrogen and the total amounts per acre for twelve months, corresponding approximately with 1908, were as follows:

Rainfall, inches.	Nitrogen per million.		Nitrogen per acre (lbs.).			% of total N.	
	as ammonia.	as nitrates.	as ammonia.	as nitrates.	Total.	as ammonia.	as nitrates.
1. 45.41	0.216	0.186	2.228	1.920	4.148	53.7	46.3
2. 28.16	0.419	0.207	2.480	1.227	3.707	66.9	33.1
3. 75.12	0.080	0.104	1.355	1.776	3.131	43.3	56.7

The total nitrogen per acre is very similar to the amounts recently found in other parts of the world, and does not seem to be influenced by the amount of rain. The relation of nitrogen as nitrates to total nitrogen, which is highest in the tropical rain at Cairns, is much lower than in New Zealand (compare Gray, *Proc. Austral. Assoc. Sydney*, 1888), where the amount of ammonia seems to be exceptionally low.

N. H. J. M.

## Analytical Chemistry.

**The Use of Trichloroethylene in Analytical Chemistry.** L. GOWING-SCOPES (*Analyst*, 1910, 35, 238-245).—Trichloroethylene, known in commerce as "Westrosol," is a colourless, readily volatile, and non-inflammable liquid, b. p. 88°. It dissolves practically all organic compounds that do not contain two or more carbonyl or hydroxyl groups, also some inorganic substances. It may be used for the extraction of fat in milk and similar products; the residue should be well rubbed with sand, and every trace of moisture be absent before extracting in the Soxhlet apparatus.

The solvent properties resemble those of chloroform and carbon tetrachloride. It withstands the action of alkalis, but being an unsaturated compound it cannot be employed in presence of oxidising agents.

L. DE K.

**Burette with Automatic Filling Arrangement.** EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1910, 24, 234—236).—The vertical stopcock of the burette is also connected with a siphon tube leading to the stock bottle containing the liquid used in the burette, and raised to a level such that the opening of the tube in the stock bottle is at the same level as the zero-mark of the burette. The stopper is bored in the ordinary way for connexion with the burette, but on the opposite side is a cavity of such a size that on turning the stopper through 180° from the position when the tap is open to the burette, connexion is made between the stock bottle and the burette. The latter then fills automatically.

T. S. P.

**An Adjustable Automatic Burette.** J. D. ROSE (*J. Amer. Chem. Soc.*, 1910, 32, 703—704).—Two tubes are connected at their lower ends by a four-way stopcock to the supply tube above and the delivery tube below. The stopcock is bored in such a manner that the exit of a hole is 90° from the entrance; 90° further around is the entrance of the other hole, which in turn is the same distance from its exit. Each passage can, therefore, be made to communicate with either side of the burette by simply turning the stopcock one-quarter turn to the right or left. The position of the hole permits the filling of one side and the emptying of the other simultaneously, so that while one charge is being delivered another is being measured.

The control of the liquid is secured by means of open floats containing a little mercury, which acts as a seal on the bottom of a glass tube; these tubes allow the passage of air to and from the burette. They are adjustable up and down, and permit of the calibration of the pipette in any desired quantities.

The liquid is taken from the supply bottle by means of a siphon or tubulature at the bottom. In either case a stopcock is interposed between the supply and the burette as a precaution.

L. DE K.

**Modification of Nowicki's Gas-absorption Pipette.** LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1910, 24, 233—234).—The bulb containing the spiral in Nowicki's apparatus (*Abstr.*, 1905, ii, 760) has been made shorter and wider, with the result that for the same length of spiral the inclination of each turn to the horizontal is considerably diminished. The gas thus passes more slowly through the spiral, and the absorbing effect is better. A subsidiary opening has also been provided towards the centre of the spiral, so that when the surface of the absorbing liquid falls below the top end of the spiral, the circulation of liquid will take place through this subsidiary opening.

T. S. P.

**Modification of the Winkler-Hempel Gas Burette.** LUCIEN L. DE KONINCK (*Bull. Soc. chim. Belg.*, 1910, 24, 231—232).—The

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modification is similar to that already described by Gwiggner (this vol. ii, 445), except that the capillary tube which puts the burette in connexion with the pipette is horizontal instead of vertical.

T. S. P.

**Gas Analysis by Condensation.** ERNST ERDMANN and H. STOLTZENBERG (*Ber.*, 1910, 43, 1702—1707).—The method consists in submitting the gas to be analysed to such a temperature that one constituent is completely liquefied (or solidified). The uncondensed gas is then completely separated (for apparatus used, see succeeding abstract) and its volume measured. The condensed gas is allowed to vaporise, and its volume measured.

The method possesses the advantage that the constituents of the gaseous mixture are separated without being absorbed, and can be tested as to their purity. Moreover, it offers a check on the accuracy of working, since the sum of the volumes of the gaseous constituents must be equal to the volume of the original mixture. It can only be used, however, when the vapour pressure of the higher boiling constituent is negligible at the boiling point of the lower boiling constituent.

Accurate analyses of the following gaseous mixtures were made, the condensing agent being indicated in each case. Ethylene and hydrogen (liquid air,  $-190^{\circ}$ ); ethylene and oxygen, or air (liquid oxygen,  $-183.7^{\circ}$ ), the condensation of the ethylene being allowed to take place under slightly diminished pressure; carbon dioxide and oxygen (pentane bath at  $-130^{\circ}$ ); nitrous oxide and oxygen (pentane bath at  $-155^{\circ}$  to  $-160^{\circ}$ ).

T. S. P.

**Apparatus for Gas Analysis by Condensation.** H. STOLTZENBERG (*Ber.*, 1910, 43, 1708—1710).—The apparatus consists essentially of three gas burettes and levelling tubes, similar in shape to the Hempel burettes, and a glass tube bent into the shape of a Y, so that the stem of the Y, which is bent into a number of S-shaped curves, can be immersed in the condensing liquid. The internal diameter of the tube is 1.5—2 mm. The gas to be analysed must be dry, and mercury is used as the measuring liquid.

Two burettes (A and B) are placed on one side of the condensing tube, and are so arranged that they may be used as a mercury pump for extracting and collecting uncondensed gas from the apparatus. The third burette (C) is placed on the other side of the condensing tube, and is used for measuring the gaseous mixture, and also the constituent gases.

The method of procedure is as follows: The gas to be analysed is measured in C, the remainder of the apparatus being full of mercury. It is then passed backwards and forwards through the condensing tube, which is immersed in the appropriate condensing liquid until condensation is complete, four such passages backwards and forwards being generally sufficient. The uncondensed gas is then pumped into A, the condensed gas allowed to vaporise, and forced into C, where it is measured, there being the necessary stopcocks for separating the various parts of the apparatus from each other. C is then emptied,

the uncondensed gas transferred to it from A, and its volume measured.

T. S. P.

**Estimation of Iodine in Protein Combinations.** LOUIS W. RIGGS (*J. Amer. Chem. Soc.*, 1910, 32, 692—698. Compare Abstr., 1909, ii, 504, 699).—A confirmation of the author's previous statement that in Baumann's process (fusion of the protein matter with sodium hydroxide and potassium nitrate) a little iodate is formed, which thus escapes detection. The acidified solution, after removing the iodine liberated with chloroform or, preferably, carbon tetrachloride, must, therefore, always be tested for iodine by Devarda's reduction process.

L. DE K.

**Estimation of Small Quantities of Iodine, with Special Reference to the Iodine Content of the Thyroid Gland.** ANDREW HUNTER (*J. Biol. Chem.*, 1910, 7, 321—350).—The material is fused with a mixture of anhydrous potassium carbonate, anhydrous sodium carbonate, and potassium nitrate; the iodine is then estimated by Dupré's method, which consists in converting it quantitatively into iodic acid by the addition of chlorine water; the point at which the iodine is completely converted can be determined quite sharply by the disappearance of the starch or chloroform reaction. The method is stated to be more expeditious and accurate than Baumann's.

W. D. H.

**The Exact Estimation of Sulphur in Soluble Sulphates.** EUGENE T. ALLEN and JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1910, 32, 588—617).—To 350 c.c. of the solution containing about 1 gram of an alkali sulphate are added 2 c.c. of hydrochloric acid, and the liquid is heated to boiling. A sufficiency of barium chloride is now added at once, and the precipitate collected and treated as usual. Although the results are accurate, this is only caused by a compensation of errors. It is, therefore, better to precipitate the solution slowly by adding the barium chloride drop by drop at slight intervals, and to filter after the whole has remained for eighteen hours. The barium precipitate, after ignition, is not pure, and to get the correct weight, reference must be made to tables given in the original paper; the corrections vary according to the exact nature of the solution.

Barium sulphate may be freed from occluded alkali sulphate by dissolving in hot sulphuric acid and pouring the solution into water. The liquid contains the soluble sulphates, which may be recovered in the usual manner, and finally converted into barium sulphate.

L. DE K.

**Detection and Estimation of Sulphurous Acid in Wines.** L. MATHIEU (*Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 1093—1096).—The presence of free and combined sulphurous acid in wine may be detected by treating 20 c.c. of the sample with about 1 gram of a mixture consisting of 4 grams of barium chloride, 20 grams of citric acid, and 100 grams of barium sulphate. After the lapse of about five minutes, the wine thus treated is filtered, and a few drops of

iodine solution are added to the clear filtrate. If free sulphurous acid is present, the filtrate becomes turbid, owing to the oxidation of the sulphurous acid, the resulting sulphuric acid combining with the excess of barium chloride in the solution. As little as 5 mg. of sulphurous acid per litre of wine yield a distinct turbidity. If the filtrate remains clear for five minutes after the addition of the iodine, heat is applied in order to oxidise the combined sulphurous acid which may be present, combined sulphurous acid not being oxidised readily by iodine at ordinary temperatures. Of course, if the wine contains free sulphurous acid, there will always be a certain amount of combined sulphurous acid present. The total sulphurous acid may be estimated by distilling a portion of the wine in an atmosphere of carbon dioxide, and collecting the distillate in a definite volume of standard iodine solution, the excess of iodine being then titrated with arsenious acid solution. Another portion of the wine is distilled in a similar way, after the free sulphurous acid has been oxidised by the addition of iodine, followed by an addition of arsenious acid; the combined sulphurous acid is thus obtained in the distillate. The difference between the quantities of combined and total sulphurous acid found, gives the amount of free sulphurous acid present. W. P. S.

**Detection of Sulphuric and Phosphoric Acids in Wines.** A. HUFERT and F. ALBA (*Ann. Chim. anal.*, 1910, 15, 223—228).—Results of a series of experiments carried out by the authors show that plastered wines contain potassium hydrogen sulphate; the detection of the latter substance is, therefore, of little use as a means of distinguishing a plastered wine from one to which sulphuric acid has been added. Plastered wines contain more calcium sulphate and calcium tartrate than do normal wines and those containing sulphuric acid. It does not seem to be possible to distinguish between wines treated with calcium hydrogen phosphate and those to which phosphoric acid has been added. In both cases the alkalinity of the ash is diminished, calcium hydrogen phosphate possibly having slightly the greater effect in this direction. W. P. S.

**Quantitative Distillation of Ammonia by Aeration. II.** PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1910, 32, 689).—Further remarks on the apparatus described previously (*Abstr.*, 1907, ii, 776), and a reply to criticisms.

The residue in the Kjeldahl flask is diluted with four volumes of ammonia-free water. When cold, the flask is connected with the absorption bottle, and, after reducing the rate of aeration, saturated alkali hydroxide is added in large excess, and the flask is shaken at the same time in a rotary fashion. The time required for the complete expulsion of the ammonia is at most three hours.

L. DE K.

**Estimation of Nitrogen as Ammonia.** ACH. GRÉGOIRE (*Bull. Soc. chim. Belg.*, 1910, 24, 221—223).—Instead of the usual method of distilling ammonia into excess of standard acid and titrating the excess of acid, the author recommends that the ammonia should be collected



in a special absorption apparatus, consisting of four bulbs containing distilled water, and then titrated directly with standard sulphuric acid. Indicators, such as methyl-orange, or even rosolic acid, then give a very sharp end-point.

T. S. P.

**Influence of Chlorine on the Estimation of Nitric Nitrogen.** ROBERT STEWART and J. E. GREAVES (*J. Amer. Chem. Soc.*, 1910, 32, 756-757).—It is already known that the estimation of nitrogen, existing as nitrates, by the phenolsulphonic acid method is affected by the presence of chlorides. In the course of an investigation of the influence of irrigating water on the movement and production of such nitrogen in the soil, a careful study of this question has been made. It has been found that when chlorine is present in as small a quantity as 2.638 parts per million, the estimation of nitric nitrogen gives low results, and that in the presence of larger amounts of chlorine, the results may be as much as 10% too low.

E. G.

**Estimation of Nitrites and Nitrates by the "Sulphophenol" Reagent.** ISIDORE POUGET (*Bull. Soc. chim.*, 1910, [iv], 7, 449-452).—Usually the Grandval and Lajoux process is used for the estimation of nitrates only, but it is known that the reagent (phenol dissolved in sulphuric acid) is affected by nitrites (compare Farcy; this vol., ii, 72), and it is now shown that the colour produced by a given quantity of nitrite is equivalent to that which would be produced by one-third the equivalent quantity of nitrogen, if this were present as nitrate.

Nitrites are decomposed by sulphuric acid in accordance with the equation:  $3\text{HNO}_2 = 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$ . Consequently, in applying the Grandval and Lajoux process to a mixture of nitrite and nitrate, the colour due to the nitrate is enhanced by that formed from the nitrite, and the quantity of nitrate originally present is given by the expression  $N - n/3$ , where  $N$  is the total nitrate found, and  $n$  the amount of nitrite, which must be determined previously.

A colorimeter with dipping prisms should be used for comparing tints, and a blue glass screen facilitates comparison. Chlorides, if present, should be eliminated by precipitation with silver sulphate before applying the process. If the original solution is dark coloured, due to organic matter, it may be cleared by means of freshly-precipitated lead oxide. The best results are obtained with liquids containing the equivalent of 0.03 to 0.3 milligram "nitric" nitrogen, the solution for comparison containing 0.1 milligram.

T. A. H.

**Estimation of Nitric Nitrogen as Ammonia.** C. FRABOT (*Ann. Chim. anal.*, 1910, 15, 219-223).—The author has investigated various reduction methods for the estimation of nitrates, and finds that simple reduction with aluminium in alkaline solution yields accurate results, and that the process recommended by Salle (this vol., ii, 451) is equally trustworthy. The method described by Pozzi-Escot (this vol., ii, 155) appears to be an unnecessary complication of the original aluminium process.

W. P. S.

\* **The Nitrogenous Substances Present in Bone Superphosphate.** GASTON CHARDET (*Ann. Chim. anal.*, 1910, 15, 215-219).—Nitrogen is present in bone superphosphate as humic nitrogen, amine-

nitrogen (glycine, leucine, alanine), basic nitrogen (arginine, lysine, histidine), ammonia, and in the form of undecomposed proteins. The latter are of less value as a manure than the humic substances, etc., and, as it is desirable to know in what proportions the various nitrogenous substances are present in superphosphate, the following methods are described for the estimation of the different groups. *Ammonia* is estimated by distilling the phosphate in the presence of magnesia. *Humic, basic, and amino-nitrogen*.—Fifty grams of the superphosphate are heated on a water-bath for thirty minutes with 150 c.c. of 90% alcohol and 15 c.c. of ammonia, the solution is then filtered, and the residue is washed with 250 c.c. of alcohol containing 5 c.c. of ammonia; the filtrate and washings being diluted with alcohol to a volume of 500 c.c. Two hundred c.c. of this solution are evaporated to expel the alcohol, the residual solution is treated with a slight excess of barium hydroxide, again boiled, and the precipitate formed is collected on a filter, washed with water, and the nitrogen is estimated in it by Kjeldahl's method; the quantity of nitrogen found represents the humic nitrogen. The filtrate from the barium hydroxide precipitate is acidified with hydrochloric acid and treated with phosphotungstic acid, which precipitates the basic nitrogenous substances present. The filtrate from the tungstic acid precipitate is evaporated, and the amino-substances are estimated in the residue by Kjeldahl's method. The residue remaining insoluble in ammoniacal alcohol contains the proteins, and the latter are estimated in a portion of the dried residue after the ammonia has been removed by boiling in the presence of magnesia. The following percentage quantities of nitrogen were found in four samples of bone superphosphate examined: total nitrogen, 0.78—2.10; ammoniacal nitrogen, 0.03—0.08; humic nitrogen, 0.04—0.11; basic nitrogen, 0.11—0.31; amino-nitrogen, 0.38—1.12; protein nitrogen, 0.18—0.48. W. P. S.

**Gravimetric Estimation of Phosphates.** A. H. MAUDE (*Chem. News*, 1910, 101, 341).—Woy's process (weighing as phosphomolybdic anhydride: *Abstr.*, 1898, ii, 138) is recommended. L. DE K.

**Estimation of Carbon in Steel by means of Allihn's Filter Tube.** PRETTNER (*Chem. Zeit.*, 1910, 34, 578—579).—The crude carbon is separated in the usual manner by boiling the steel with copper chloride, etc., and collected in an Allihn filter tube, which also serves as the combustion tube. After being dried at 110—120°, the carbon is burnt in a current of purified oxygen, and the carbon dioxide absorbed in Dennstedt's soda-lime apparatus. As, however, there is always formed a certain amount of carbon monoxide, the oxygen, after leaving the Allihn tube and traversing a calcium chloride tube, is passed through a 25—30 cm. long quartz tube filled with copper oxide spirals, and heated to redness. Two burners only are required, one for each tube. After leaving the absorption apparatus, the oxygen passes through a 60 cm. long rubber tube into a small bottle containing water, so as to be able to regulate the number of bubbles passing through. L. DE K.

**The Mercury Cathode in Rapid Electro-analysis.** W. S. KIMLEY (*J. Amer. Chem. Soc.*, 1910, 33, 637—641).—In the process recommended by the author, the amalgam is formed and weighed in the same flask, as the transfer of the amalgam to a special weighing flask is sometimes attended with loss.

A platinum wire is sealed into the bottom of a round-bottomed flask holding about 125 c.c., and when 40 grams of mercury are introduced, the whole weighs about 65 grams. When the deposition is complete, the solution is siphoned off as far as possible without breaking the circuit, the flask is filled with water, and this is repeated until the current drops nearly to zero. The flask is then removed from the stirrer, and the liquid removed by a glass tube drawn out to a point and attached by a rubber tube to the suction tube of a filter pump. After thoroughly washing with water, and the last drops having been removed, the amalgam is washed with alcohol, then with ether, and the last traces of this are removed by placing the flask in a water-oven.

A convenient cell when dealing with a small volume of liquid is described.  
L. DE K.

**The Filtrate from the Precipitate with Hydrogen Sulphide [in Qualitative Analysis].** JULIUS PETERSEN (*Zeitsch. anorg. Chem.*, 1910, 67, 253—256).—An improved method of qualitative analysis after removal of the hydrogen sulphide precipitate. Barium and strontium are precipitated with sulphuric acid, and sodium carbonate, sodium sulphide, and sodium hydroxide are then added. The filtrate contains only aluminium. The residue is dissolved in hydrochloric acid to which a little sodium sulphide is added. Cobalt and nickel sulphides remain insoluble. The filtrate is boiled to remove hydrogen sulphide, and sodium carbonate and hydroxide are added. Only zinc goes into solution. The residue is treated with sodium peroxide, and heated momentarily to boiling. Chromium is thus removed as chromate. The residue is now dissolved in hot 5% acetic acid, containing 5% of sodium phosphate. Calcium and magnesium are dissolved, whilst iron and manganese remain insoluble. A shortened form of the scheme is applicable if cobalt, nickel, and chromium are known to be absent.  
C. H. D.

**The Detection and Estimation of Very Small Quantities of Silver.** G. STAFFORD WHITEY (*Zeitsch. anorg. Chem.*, 1910, 67, 62—64).—Several organic compounds, such as sucrose, starch, dextrin, cellulose, and glycerol, yield a dark coloration with silver salts in presence of sodium hydroxide, owing to the formation of colloidal silver.

Fifty c.c. of the very dilute silver solution are taken, a few drops of a concentrated solution of sucrose are added, the beaker is placed in boiling water for two minutes, and, after adding 6 drops of  $N/1$  sodium hydroxide, the heating is continued for twenty to thirty seconds. After cooling, the solution is transferred to a Nessler tube and compared with a standard. The quantity of silver that may be thus detected is 0.000002 gram in 50 c.c. The sensitiveness is equal to

that of the nephelometer (Richards and Wella, *Abstr.*, 1904, ii, 287), and the reaction may thus be employed in atomic weight estimations. Ammonia must be absent, but copper, zinc, mercury, bismuth, cadmium, and lead are without influence if not present in sufficient quantity to yield visible precipitates with the alkali. C. H. D.

**Rapid Estimation of Copper in Coarse Metal.** BR. WINKLER (*Chem. Zeit.*, 1910, 34, 603).—One gram of the powdered sample is heated in a 100 c.c. flask with 10 c.c. of strong nitric acid and 10 c.c. of sulphuric acid on a sand-bath until sulphuric fumes appear. When cold, a little water is added, and the whole is heated until a clear solution is obtained. Any arsenic is oxidised by addition of 0.5 gram of potassium chlorate. The iron is precipitated by ammonia, and when cold the solution is diluted to the mark, shaken, and filtered. Fifty c.c. of the filtrate are then acidified with sulphuric acid, 3 grams of potassium iodide are added, and the liberated iodine is titrated with thiosulphate as usual; it is advisable to check this by means of pure metallic copper.

In the case of ores. 2 grams are taken and heated with 10 c.c. of nitric, 5 c.c. of hydrochloric, and 15 c.c. of sulphuric acid, and treated further as directed. L. DE K.

**Application of the "Aluminium Reaction" in the Analysis of Mercuric Compounds.** C. REICHARD (*Pharm. Zentr.-h.*, 1910, 51, 443—449).—Further particulars as to the corrosive action of soluble mercury salts on aluminium foil (formation of a characteristic stain of aluminium hydroxide: *Abstr.*, 1907, ii, 691).

Free acids should be absent. Although the test is, as a rule, given by soluble salts only, there are exceptions, as mercuric iodide also gives the reaction; mercuric sulphide will cause a stain on aluminium if struck with a hammer, but in analytical practice it should be converted into the chloride.

The aluminium foil should be absolutely free from greasy matter; in this case the reaction is astonishingly delicate.

A mixture of dry mercuric chloride and copper, or cadmium sulphate, also causes the stain to appear, but in solutions containing these metals the test fails. L. DE K.

**Volumetric Estimation of Mercury in Galenical Preparations.** R. GÄTTER (*Pharm. Zeit.*, 1910, 55, 427—428).—The author describes the process used in the titration of mercuric chloride in the Neisser-Siebert lotion used for disinfecting purposes, which contains a large amount of colloidal matters.

45.16 Grams of the preparation are diluted with 250 c.c. of water, and introduced into a 750 c.c. stoppered flask. After shaking vigorously for a few minutes, a solution of 5 grams of potassium iodide is added, and the whole again shaken for ten minutes, when 50 c.c. of 10% sodium hydroxide and 20 c.c. of 40% formaldehyde are added. After shaking gently for ten minutes, 12 c.c. of glacial acetic acid are added, and then 15 c.c. of *N*/10-iodine. After again shaking for ten minutes, the excess of iodine is titrated with *N*/10-sodium thiosulphate.

Ten c.c. of *N*/10-iodine taken up represent 0.135 gram of mercuric chloride.  
L. DE K.

The Estimation of Mercury in Urine and Fæces. CONRAD SIEBERG (*Biochem. Zeitsch.*, 1910, 25, 328—332).—The organic matter is destroyed by the Neumann process, and the mercury precipitated as sulphide and weighed. The author gives full experimental details.  
S. B. S.

Volumetric Estimation of Cerium in Cerite and Monazite. FLOYD J. METZGER and M. HEIDELBERGER (*J. Amer. Chem. Soc.*, 1910, 32, 642—644).—An application of the process described by Metzger to the analysis of cerite and monazite (oxidation with sodium bis-muthate, reduction of the ceric salt with ferrous sulphate, and titration of the excess of iron with standard permanganate: *Abstr.*, 1909, ii, 626).

In the case of cerite, 0.5 gram of the finely-powdered sample is fused with potassium pyrosulphate, and the mass dissolved in 350 c.c. of water containing 5 c.c. of sulphuric acid. In the case of monazite, 0.6 gram of the sample is heated for six hours with sulphuric acid in a porcelain dish, and then poured into 350 c.c. of cold water. In either case the solution is filtered, heated to boiling, and mixed with 100 c.c. of saturated solution of oxalic acid. The precipitate formed, which includes the cerium, is then washed and treated as follows:

(1) It is washed off the filter with water, dissolved by means of 20 c.c. of sulphuric acid, 5 grams of ammonium sulphate are added, and, after diluting to 100 c.c., the liquid is boiled with sodium bismuthate as directed previously. This process gives satisfactory results if the amount of oxalates is but small; hardened filters are recommended.

(2) The filter containing the oxalates is burnt, finally over the blast lamp. The oxides are then heated with 10 c.c. of sulphuric acid, and when cold poured into 100 c.c. of water; if no solution takes place, another 10 c.c. of acid are added, and the liquid is heated until a clear yellow solution is obtained. After diluting to 100 c.c., 2 grams of ammonium sulphate are added, and oxidation is effected with 1 gram of sodium bismuthate.

(3) The oxalates are boiled with aqueous sodium hydroxide, and the washed precipitate is dissolved in dilute sulphuric acid and then treated as directed in (2). This method is by far the best.  
L. DE K.

Eosin Reaction of Glass at Fractured Surfaces. II. FRANZ MYLIUS (*Zeitsch. anorg. Chem.*, 1910, 87, 200—224. Compare *Abstr.*, 1907, ii, 910).—The method of studying the "weathering" qualities of glass by means of iodoeosin has now been extended to the heavier optical glasses. A microchemical method of analysing such glasses quantitatively is described. The bases of glass absorb eosin from its ethereal solution, but silica or boric acid do not. Alumina has a slight action. Pure lead silicate absorbs slowly, basic silicate rapidly. Long immersion of the heavier glasses in the solution causes

increased absorption which is not proportional to the weathering, but immersion for one minute in a solution containing 0.5 gram of iodoecsin per litre gives a true measure of the alkalinity of the glass. For weathering experiments, the glass is kept, with the fractured surface uppermost, in a vessel containing moist air. Under these conditions, the alkalinity of heavy glasses decreases during weathering, becoming constant after about a week. The values of the alkalinity for different glasses after this time are comparable with one another.

A concentrated solution of sodium silicate, mixed with lead oxide, sets to a hard mass. A more dilute solution yields a colloidal solution, which coagulates at 50°, and a similar solution is obtained from ignited silica, lead oxide, and a cold solution of sodium hydroxide. The action of water on lead glass consists in the formation of a concentrated solution, which contains all the constituents of the glass. Further addition of water causes hydrolysis and the formation of colloids, which then coagulate, depositing a layer of gelatinous silicates. The only portion of the glass which is then reactive towards iodoecsin is the alkali produced by hydrolysis, and converted into carbonate in the process of weathering. The decrease in alkalinity during weathering is greatest in glass containing a large proportion of lead oxide. The decrease is still more strongly marked in barium glasses, and is perceptible in zinc glass. The experiments are extended to twenty-five heavy glasses. The weathering increases with the amount of alkali, and is lessened by the presence of much baryta or zinc oxide. The replacement of silica by boric acid has little influence. Some alkaline borosilicate optical glasses weather to one thousand times the extent of stable heavy glasses.

Polished surfaces of glass require two years for a comparison of their weathering properties, and then give the same order of stability as is given by fractured surfaces in seven days. C. H. D.

The Estimation of Iron in Blood. D. CHARNASS (*Biochem. Zeitsch.*, 1910, 25, 333—340).—For clinical purposes, Jolles' colorimetric iron thiocyanate method is applicable. The colour is not directly proportional to the amount of iron present. The author gives details as to the preparation of the colour scale, and of a colorimeter for employment in the estimations. S. B. S.

Electrolytic Separation of Nickel and Cobalt. EUGENIO INERCA ALVAREZ (*Ann. Chim. anal.*, 1910, 14, 169—170).—For the estimation of nickel only, the nickel cobaltocyanide formed by the action of potassium cyanide on nickel and cobalt sulphates in presence of sulphur dioxide (0.5 gram) is dissolved in a mixture of 100 c.c. of water and 10 c.c. of ammonia, D 0.927, and 5 grams of ammonium sulphate are added. When submitted to electrolysis for two hours in the cold, D 1.00 = 0.40 ampere and 3.7—4 volts; the liquid deposits the nickel in a brilliant film free from cobalt, but containing some partly-combined carbon.

To precipitate the two metals jointly, 1 gram of nickel cobaltocyanide is dissolved in 100 c.c. of water and 50 c.c. of ammonia, and,

after adding 10 grams of ammonium sulphate, the liquid is submitted to electrolysis for one hour at 50—60°;  $DN_{100}$  = at first, 1 ampere, towards the end 1.5 ampere and 3.8 volts.

L. DE K.

**New Volumetric Method for Cobalt and Nickel.** GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1910, 32, 757—761).—A method is described for the volumetric estimation of cobalt and nickel by means of potassium ferrocyanide, which is of particular value for estimating nickel in steel.

A solution containing 20 grams of potassium ferrocyanide per litre is standardised against a cobalt or nickel solution of known strength. Three equal portions of the solution, each containing about 0.1 gram of the metal, are treated with 10 c.c. of 10% ferric chloride solution, 2—3 grams of citric acid, and a slight excess of ammonia. The solutions are then diluted to 100 c.c., and brought to a temperature of 65—75°. The ferrocyanide solution is added gradually with constant stirring, and nickel or cobalt ferrocyanide is precipitated. As the titration proceeds, a drop or two of the solution is transferred by a stirring rod to a paraffined white plate and acidified with a drop of dilute acetic acid. The solution is well stirred, and a second test made beside the first. The titration is continued until a greenish colour is developed in about five minutes at a definite point in the series. It is convenient to titrate the first portion roughly, and then to find the exact point with the other two portions. The method cannot be employed in presence of metals, such as copper, zinc, and manganese, which react with the ferrocyanide.

In order to estimate nickel in steel, 1 gram of borings is placed in a 150 c.c. flask, and 10—15 c.c. of dilute nitric acid are added. Potassium chlorate is added to the solution, which is then boiled until all the chlorine has been expelled. After repeating this treatment with potassium chlorate, the manganese dioxide is removed by filtration, and the nickel is estimated by the method already described.

The estimation of nickel in steel can also be accurately effected by the following method, which is based on those of Johnson (*Abstr.*, 1907, ii, 819) and Campbell and Arthur (*Abstr.*, 1908, ii, 779).

Steel borings (0.5 gram) are dissolved in nitric acid by the method described, and the solution is treated with 2—3 grams of citric acid, 2 grams of sodium pyrophosphate, and a slight excess of ammonia. The solution is diluted to 150 c.c., and cooled to 20°. A few drops of a 10% solution of potassium iodide are then added, and just sufficient  $N/10$ -silver nitrate to produce a distinct turbidity. Potassium cyanide solution, standardised by means of  $N/10$ -silver nitrate, is then slowly introduced with constant stirring until the turbidity just disappears, and the solution becomes golden-yellow. If the solution remains bright for five minutes, the titration is complete.

This method is not applicable to solutions containing large amounts of cobalt, since a peculiar dark precipitate is produced during the titration which interferes with the end-reaction.

E. G.

**Estimation of Nickel in Nickel Steel.** HERMANN GROSSMANN and B. SCHÜCK (*Analyst*, 1910, 35, 247—248).—Rhead (this vol., ii, 359):

has entirely overlooked the process recommended by the authors, to which they now once more call attention.

0.5—2 Grams of nickel steel are dissolved in *aqua regia*, and evaporated on the water-bath to a volume of 10 c.c. The solution is filtered, and 15 grams of sodium potassium tartrate added for each gram of steel used in the assay; should a precipitate form, it is dissolved by a little ammonia. In the presence of much manganese, oxidation is prevented by hydrazine sulphate. Ammonia and about 40 c.c. of 20% sodium hydroxide are added, and then a cold 10% solution of dicyanodiamidine sulphate. If but little nickel is present, the precipitation takes only a short time. The precipitate is filtered through a Gooch crucible, washed with cold ammoniacal water, dried at 120—130°, and weighed.

For rapid work, however, the titration with potassium cyanide is recommended (compare Campbell and Arthur, Abstr., 1908, ii, 779).

L. DE K.

Use of Silver in the Estimation of Molybdenum, Vanadium, Selenium, and Tellurium. CLAUDE C. PERKINS (*Amer. J. Sci.*, 1910, iv, 29, 540—542; *Zeitsch. anorg. Chem.*, 1910, 67, 351—364. Compare Joch and Perkins, Abstr., 1909, ii, 932).—It has been found that molybdenum, vanadium, selenium, and tellurium may be estimated by making use of the fact that the oxides of these elements liberate iodine from an acidified solution of potassium iodide. The reactions evolved may be represented by the equations:  $2\text{MoO}_3 + 4\text{KI} + 4\text{HCl} = 2\text{MoO}_3\text{I} + 2\text{KCl} + 2\text{H}_2\text{O} + \text{I}_2$ ;  $\text{V}_2\text{O}_5 + 2\text{HCl} + 2\text{KI} = \text{V}_2\text{O}_4 + 2\text{KCl} + \text{H}_2\text{O} + \text{I}_2$ ;  $\text{SeO}_2 + 4\text{KI} + 4\text{HCl} = \text{Se} + 4\text{KCl} + 2\text{H}_2\text{O} + 2\text{I}_2$ ;  $\text{TeO}_2 + 4\text{KI} + 4\text{HCl} = \text{Te} + 4\text{KCl} + 2\text{H}_2\text{O} + 2\text{I}_2$ . The liberated iodine is estimated by shaking with specially prepared electrolytic silver in an atmosphere of hydrogen, and measuring the increase in weight of the silver. In the case of the oxides of selenium and tellurium, the increase in weight represents the iodine liberated plus the selenium or tellurium.

H. M. D.

#### Qualitative Test for Small Quantities of Gold and Silver.

ARMANI and J. BARBONI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 90—292).—It has been found that the production of coloured colloidal solutions of silver and gold by the reducing action of formaldehyde in alkaline solution can be used for the detection of very small quantities of these metals. The violet colour obtained with silver can still be recognised with certainty in the case of a solution containing 1 part of silver in 200,000 parts. The sensitiveness of the reaction in the case of gold is of the same order. If, however, the solution contains less than 1 part of gold in 100,000 parts, the violet colour is not developed until the solution is boiled. The tests are recommended for the detection of silver and gold on plated goods. In the case of plated copper or brass articles, these are treated with a mixture of 1 part of nitric and 9 parts of sulphuric acid, which removes silver, but has no action on copper or brass. In testing for gold, the material is treated with nitric acid, the insoluble residue is then digested with *aqua regia*, heated to dryness with sulphuric acid, and the residue dissolved in a small quantity of water.

H. M. D.



**Oxidation of Organic Matter by Potassium Permanganate.** EDMOND POPPE (*Bull. Soc. chim. Belg.*, 1910, 24, 237—239).—In determining the organic matter present in water by the permanganate method, it is usual, according to the method of Knbel and Tiemann, to calculate the quantity of organic matter by multiplying the weight of permanganate used by five. The author tests this on aqueous solutions of thirteen organic compounds (various sugars, acids, etc.), and finds that the factor 5 is very far from correct. Moreover, the actual oxidising power of potassium permanganate in acid solution with respect to these organic substances is not equal to the theoretical. The temperature and time over which the experiments lasted are not stated. T. S. P.

**Determination of the Source of Naphtha or its Derivatives.** N. CHERCHEFFSKY (*Compt. rend.*, 1910, 150, 1338—1341).—Naphtha is fractionated below 300° until one-twentieth of the volume has been collected, and the following constants determined in the distillate: (1) Density at 15°; (2) mean b. p.; (3) index of refraction; (4) solubility-coefficient; (5) iodine number; (6) temperature at which a hot alcoholic solution becomes turbid when cooled in a sealed tube; (7) temperature at which a hot mixture of the oil with acetic anhydride becomes turbid when cooled in an open tube. The author gives in tabular form the foregoing data for a number of naphthas from different localities, and states that they may be used to determine the origin of commercial naphthas, and to give some information as to their composition. W. O. W.

**Estimation of Blood-Sugar.** LEONOR MICHAELIS and PETER RONA (*Zitsch. physiol. Chem.*, 1910, 67, 104).—Remarks in reference to the paper by Bang, Lyttkens, and Sandgren (this vol., ii, 554), who have not given the present authors due credit for their work. W. D. H.

**The Most Simple Method for the Estimation of Dextrose in Urine.** FRANZ LEHMANN (*Apoth. Zeit.*, 1910, No. 25. Reprint, 3 pp.).—A slight modification of the process described previously (*Abstr.*, 1909, ii, 442), the clarification of the urine by means of basic lead, acetate, and sodium carbonate being omitted. After boiling with excess of Fehling's solution, the excess of copper is estimated by de Haen's iodometric process.

A convenient table is given to facilitate the calculation of the sugar content. L. DE K.

**Analysis of Artificial Honey.** F. MUTTELET (*Ann. Palsif.*, 1910, 3, 206—207).—Artificial honey may be detected, even when mixed with natural honey, by means of Fiehe's test, which depends on the red coloration produced when resorcinol in hydrochloric acid solution is allowed to act on  $\beta$ -hydroxy- $\delta$ -methylfurfuraldehyde; the latter substance is always present in small quantity in invert sugar which has been prepared by heating sucrose in the presence of an acid. In carrying out the test, the honey is shaken with ether, and the

spherical extract is allowed to evaporate spontaneously in a china basin. The residue obtained is then treated with a few drops of the reagent (1 part of resorcinol dissolved in 100 parts of hydrochloric acid, D 1.19). The appearance of a distinct cherry-red coloration denotes the presence of invert sugar in the sample. Natural honey may yield a yellowish-orange coloration with the test. W. P. S.

**Apparatus for the Estimation of Cellulose.** ACH. GRÉGOIRE and EM. CARPIAUX (*Bull. Soc. chim. Belg.*, 1910, 24, 217—221).—The authors describe a modification of Stiff's apparatus (Abstr., 1896, ii, 9) for estimating cellulose in foodstuffs according to the method of Jenneberg and Stohmann. The neck of a pear-shaped flask, open at both ends, is fitted into a Gooch crucible by means of rubber. The Gooch crucible is charged with quartz and a layer of asbestos fibre, and is fitted into a thistle funnel for convenience of filtration. The foodstuff to be analysed is treated in the pear-shaped flask with sulphuric acid and alkali in succession, the contents of the flask being heated by a jet of steam, and the asbestos in the crucible kept in position meanwhile by a glass ram-rod. During this treatment, filtration is prevented by attaching rubber tubing to the thistle funnel, and raising the end to an appropriate height. After the treatment is complete, filtration is allowed to take place at atmospheric pressure. The succeeding operations are carried out as usual.

Twelve estimations can be made in one day, whereas the old methods would have required at least four days; the results are satisfactory. T. S. P.

**Estimation of the Volatile Acids in Wines by means of Böttcher's Apparatus.** THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1910, 19, 484—486).—The Böttcher apparatus (Abstr., 1907, ii, 38) is recommended particularly in laboratories where the analysis of wines is not of frequent occurrence.

The addition of a few drops of oil free from acidity is a good device to prevent foaming during the distillation. L. DE K.

**Quantitative Colorimetric Estimation of Small Quantities of Hydrocyanic Acid.** ERNST BERL and MAX DELPY (*Ber.*, 1910, 38, 1430—1431).—A method for the estimation of hydrogen cyanide in amounts ranging from 0.004 to 0.00004 gram per c.c.

The solution to be estimated is made alkaline with potassium hydroxide (1:1), a large excess being avoided, and then a solution of ferrous sulphate (1:30) containing oxide added, so that there are at least 10 mols. of ferrous sulphate to 1 mol. of hydrogen cyanide. The mixture is left for ten minutes at room-temperature, being well shaken from time to time, then boiled for two to fifteen minutes, cooled, and 0.5% hydrochloric acid added until acid. A precipitate of Prussian blue forms gradually. After five hours, if the original solution is colourless, the whole is made up to 100 c.c., well shaken, and the colour of the suspensions compared in a Krüss colorimeter with standards made from potassium cyanide solutions of known strength. When the

supernatant liquor is strongly coloured after the Prussian blue precipitate has settled, it is decanted off and replaced by water.

Very dilute cyanide solutions, for example, 0.00004 gram HCN per c.c., are first acidified, extracted with ether, and the ethereal extract shaken with a small quantity of potassium hydroxide solution, whereby a cyanide solution is obtained of such strength that the above method can be used. T. S. P.

**Estimation of Tartaric Acid in Natural Products.** CONSTANTIN BEYS (*Compt. rend.*, 1910, 150, 1250—1251).—The following process is stated to give better results than any method hitherto described.

After heating for thirty minutes 1—2 grams of the substance with its own weight of 5% sulphuric acid, 5 volumes of alcohol are added and 10 volumes of ether. The precipitate is filtered off, and washed with alcohol and ether in the same proportions. The filtrate is neutralised with 90% alcoholic potassium hydroxide, and then treated with 5—10 c.c. of the same solution. After heating to 38° and cooling, the liquid A is decanted from the precipitate B, and acidified with glacial acetic acid; the potassium hydrogen tartrate which separates is washed with 96% alcohol. The precipitate B is brought into solution with 12—15 c.c. of hot water, and treated with 5 c.c. of acetic acid; after shaking for five minutes, alcohol is added in amount equal to 65% of the volume of liquid. The precipitate is washed successively with 65% and 96% alcohol, added to the precipitate from A, and the whole titrated according to Goldenberg's method (*Abstr.*, 1908, ii, 237), using phenolphthalein as indicator. W. O. W.

**Formaldehyde Titration of Amino-acids in Urines.** HANS MALFATTI (*Zeitsch. physiol. Chem.*, 1910, 68, 152—164. Compare *Abstr.*, 1909, ii, 837).—The urine, after removing phosphates as directed in the author's previous paper, should be made neutral to phenolphthalein before starting the formaldehyde titration. The first change to very faint pink should be taken as the end-point. It is also pointed out that the process, although suitable for clinical purposes, is not sufficiently accurate for scientific work. L. DE K.

**Estimation of the Lecithin-content of Soja-oil.** M. RIEGER (*Pharm. Zeit.*, 1910, 55, 428).—The author extracts the crude lecithin from lecithin containing preparations by means of boiling methyl alcohol, and in the residue left on evaporation the phosphoric anhydride is estimated in the usual way. This multiplied by 11.36 represents pure lecithin. Soja-oil was found to contain 0.15% of this substance. L. DE K.

**Use of Urotropin for "Desulphurising" Wines and Musts.** HENRI FONZES-DIAON (*Bull. Soc. chim.*, 1910, [iv], 7, 389—390).—Urotropin having come into use for "desulphurising" treated wines, the reaction described by Denigès (this vol., ii, 357) has been recommended officially for the detection of formaldehyde in such wines.

The author has already suggested the estimation of ammonia liberated by magnesia from wines as an additional means of ascertaining whether urotropin has been added to them. Denigès' colour reaction is only satisfactory when care is taken to have enough sulphuric acid present. He also points out that in applying Blarez's reaction (*Bull. Soc. Pharm. Bord.*, February 1910), depending on the reddish colour given by formaldehyde with phenylhydrazine hydrochloride, care must be taken to use for the initial distillation a fairly large volume of wine, slightly acidified with sulphuric acid. If too much acid is used or the distillation is carried too far, some formaldehyde is formed by the action of the acid on components of the wine.

T. A. H.

**Estimation of Aldehydes in Alcohol. Preparation of Standard Aldehyde Solution.** LÉON RONNET (*Ann. Falsif.*, 1910, 3, 205—206).—Standard aldehyde solution for use in the colorimetric estimation of aldehydes may be prepared from aldehyde-ammonia after the latter has been washed with ether and dried over sulphuric acid. The aldehyde-ammonia must not be dried under reduced pressure over sulphuric acid, as in this case it undergoes decomposition and is converted into ethylideneimine, which in turn polymerises to form a triple molecule. Pure acetaldehyde may also be prepared by distilling a mixture of paraldehyde and concentrated sulphuric acid.

W. P. S.

**New Method for Estimating the Three Methylamines and Ammonia in Mixtures.** JEAN BERTHEAUME (*Compt. rend.*, 1910, 150, 1251—1253. Compare Abstr., 1908, ii, 742).—After criticising adversely Bresler's method (*Ann. Chim. anal.*, 1901, 6, 28), the author gives details of a process based on the insolubility of ammonium chloride and methylamine hydrochloride in chloroform. These two salts are then estimated by Francois' method (Abstr., 1907, ii, 391, 303.), and the di- and tri-methylamine remaining in chloroform solution separated by taking advantage of the greater insolubility of tri-methylamine periodide in water.

W. O. W.

**A Modification of the Nitrometer for Estimating Urea.** GUSTAV MOSSLER (*Chem. Zentr.*, 1910, i, 1180—1181; from *Zeitsch. allg. österr. Apoth.-Ver.*, 1910, 48, 1—3).—The flask for the evolution of nitrogen is connected with an improved form of nitrometer, in which the adjustment to zero before an experiment is performed by opening a tap, and the adjustment of levels after the nitrogen is collected, is automatic. The original paper contains tables for the calculation of the percentage of urea.

C. H. D.

**Rapid Estimation of Albumin in Urine.** AUFRICHT (*Pharm. Zeit.*, 1910, 65, 345—346).—The results obtained by the author's method (this vol., ii, 560) come nearer to the gravimetric estimations than those obtained by the ordinary Esbach method. It is advisable to make a comparative experiment with a solution containing a definite amount of albumin, and to note the time required for complete pre-

capitation, as this differs according to the power of the centrifuge used.

Excess of urates may be removed previously by cooling. If the urine contains more than 0.5% of albumin, it should be diluted with a suitable quantity of water.

L. DE K.

**A New Method for Estimation of Fibrin Ferment and Fibrinogen in Body-fluids and Organs.** JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1910, 25, 79—83).—For estimation of the fibrin ferment varying quantities of the liquid containing the ferment are diluted to a definite volume with 1% saline and mixed with 2 c.c. of magnesium sulphate plasma, prepared by Schmidt's method, and left in a series of test-tubes on ice for twenty-four hours. The amount of the ferment-containing liquid just necessary to produce coagulation is observed. The amount of fibrin ferment is expressed by the number of times this quantity is contained in 1 c.c. The fibrinogen is determined in a similar way, only in this case the amount of ferment-containing liquid is kept constant and the amount of plasma varied. A similar system is adopted for expressing the number of fibrinogen units present.

S. B. S.

**The Guaiacum Test for Blood, and a New Modification of the Same with Sodium Peroxide.** BRUNO BARDACH and SIEGMUND SILBERSTEIN (*Zeitsch. physiol. Chem.*, 1910, 65, 511—512).—The delicacy of the guaiacum-turpentine test is much increased by the addition of alcohol; and if sodium peroxide is used instead of turpentine, this test for blood is the most delicate known.

W. D. H.

**The Value of the Guaiacum Reaction for the Forensic Detection of Blood.** J. KRATZER (*Chem. Zentr.*, 1910, i, 1458; from *Vierteljahrsschr. ger. Med. öffentl. Sanitätswesen*, 1910, 39, 42—51).—The contradictory results obtained with the guaiacum test for blood are due to the non-observance of the requisite conditions of the reaction. The guaiacum tincture should be freshly prepared, the turpentine oil must be old, and the blood solution concentrated. To fulfil these conditions, the blood is not dissolved in water, but taken up on moistened filter paper. The spot is then moistened with the guaiacum tincture, and two or three drops of turpentine oil are added. A blue colour is produced with the blood. Old samples, however, give a bright cherry-red colour with guaiacum tincture alone, which is characteristic for blood, and this reaction is not destroyed by putrefaction. The reactions should only be employed as preliminary tests.

S. B. S.

**Hæmochromogen and its Crystals.** KALMUS (*Chem. Zentr.*, 1910, i, 1458—1459; from *Vierteljahrsschr. ger. Med. öffentl. Sanitätswesen*, 1910, 39, 57—64).—The preparation of hæmochromogen crystals from blood by means of pyridine and ammonium sulphide is a valuable test, but it is also given by other agents, such as the purple-yielding bacteria. From human blood, the hæmochromogen crystals form typical

slender needles, resembling those of hæmatin. Other bloods yield other forms of crystals, although no particular form could be identified as typical for the species of animal. The instability of the crystals is the only disadvantage compared with the hæmin crystals. The hæmochromogen crystals can be readily distinguished from rust and other substances, and their formation is not readily inhibited by foreign substances, as hæmin crystals are. They can, furthermore, be examined by the microspectroscope in the violet and ultra-violet parts of the spectrum.

S. B. S.

**Hæmochromogen Test.** MITA (*Chem. Zentr.*, 1910, i, 1459; from *Vierteljahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, 39, 64-66).—To avoid the inconvenience of the separation of sulphur when ammonium sulphide is employed in the hæmochromogen test, the author employs de Dominici's 10% phenylhydrazine hydrate reagent. The crystals should be examined for double refraction. In the presence of organic matter, the blood should be first dissolved in water or acetic acid, and the solution allowed to evaporate at room-temperature. As regards the action of putrefaction or sunlight on the reaction, the hæmochromogen test is at least as trustworthy as the hæmatin test.

S. B. S.

**A Reagent for the Detection of Blood-pigment and the Preparation of Hæmochromogen Crystals.** LOCHTE (*Chem. Zentr.*, 1910, i, 459; from *Vierteljahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, 39, 66-71).—The reagent employed consisted of 10 parts of sodium hydroxide, 40 parts of distilled water, and 50 parts of 80% alcohol containing 2 parts of pyridine and 2 parts of ammonium sulphide. Six to ten c.c. of this reagent are employed for a few drops of diluted blood solution. If the red hæmochromogen solution thus obtained is shaken with air, the wine-red colour becomes yellow or brownish-yellow, according to the amount of hæmatin formed. The hæmochromogen bands thereby disappear, and are replaced by the pale band of alkaline hæmatin. The solution then reddens again, and the hæmochromogen bands reappear. This colour change can be repeated an indefinite number of times. Hydrazine sulphate can be employed in the reagent instead of ammonium sulphide, but it can then be kept only for a short time without change. The best crystals are obtainable from fresh blood when the pyridine and ammonium sulphide are added simultaneously, especially when a few drops of alcohol are added previously to fresh blood. In doubtful cases the crystals should be examined microscopically.

S. B. S.

**Use of Benzidine for the Detection of Blood and its Application in Medico-Legal Practice.** ERNST WALTER (*Deutsch. Med. Woch.*, 1910, No. 7. Reprint, 10 pp.).—The author recommends the substitution of the benzidine test for the old guaiacum test as being more decisive. Pastilles may be made containing 0.1 gram of benzidine and 0.1 gram of sodium perborate (preferable to hydrogen peroxide) and just before use such a pastille is dissolved in 10 c.c. of glacial acetic acid. The use of benzidine paper also proposed cannot be recommended. If a suspected

spot on an article of clothing, etc., is to be examined for blood, it is moistened with a drop of physiological salt solution and well rubbed with a glass rod. The drop is then absorbed in a small piece of cotton wool free from fat, and the spot at once treated with a few drops of the reagent. In presence of blood a blue coloration is noticed.

L. DE K.

**Use of Various Zinc Salts in the Detection of Urobilin.** R. WEITZ (*J. Pharm. Chim.*, 1910, [vii], 1, 533—538).—Various authors have drawn attention to the green fluorescence produced in urines containing urobilin by the addition of zinc salts (Deniges, Abstr., 1908, i, 343, ii, 200; Ruman and Delluc, Abstr., 1900, ii, 700), and have suggested this reaction as a means of detecting this substance. The author finds the following method of operating gives good results. The urine (20 c.c.) is mixed with zinc acetate (4 grams), alcohol (20 c.c.) of 95° strength is added, and the mixture shaken and filtered. The filtrate shows a marked green fluorescence if urobilin is present. The delicacy of the reaction is increased if the mixture is left from one to two hours before filtration. To liberate urobilin from the chromogen, which precedes it, the urine must be treated with a few drops of an oxidising agent, such as Gram's iodine solution, or alkaline permanganate. Mercuric sulphate should not be used as a defæcating agent before applying the test, as urobilin is liable to be lost in that way. Zinc lactate or valerate gives as good results as the acetate, but the basic carbonate is a little less delicate. Zinc sulphate or chloride may be used if their solutions are first made neutral by adding ammonia solution. Blood and biliary pigments do not interfere with this reaction, and can themselves be detected by the ordinary tests. If indoxyl is present, the urobilin should be separated by adding basic lead acetate solution, suspending the washed precipitate in alcohol, and decomposing it with dilute sulphuric acid, thus forming an alcoholic solution of urobilin to which, after exact neutralisation by ammonia, the test may be applied.

T. A. H.

**The Detection of Peptolytic Enzymes in Animal and Vegetable Tissues.** EMIL ABDEGHALDEN (*Zeitsch. physiol. Chem.*, 1910, 66, 137—139).—An easy method for the detection of peptolytic enzymes consists in placing sections of the tissue in solutions of silk-peptone; after a few hours' digestion tyrosine crystals are found adhering to the sections if a peptolytic enzyme is present. Possibly the injection of the silk peptone into the organ and subsequent examination of it may throw light on the question as to what cells are concerned in the formation of the enzyme, and differences may be found in normal and pathological conditions. The enzymes in question were found in all the animal and vegetable tissues examined; in plants, the amount as judged by the yield of tyrosine is small. The method may be used in plants to determine the date when such enzymes appear during germination. Another microchemical reaction which gives good results is to use polypeptides which contain tryptophan; the violet reaction with bromine water does not occur until tryptophan is liberated.

W. D. H.

**Comparison of Results Given by Acidity Determinations and by Catalasimetry in Estimating the Freshness of Milk.** J. SARTOU (*J. Pharm. Chim.*, 1910, [vii], 1, 387—393).—Soxhlet's observation that milk only undergoes lactic fermentation after a period of incubation, is confirmed. In a series of trials with milks kept in the laboratory, it was found that the acidity remained constant during the first forty-two hours, whilst catalytic action on hydrogen peroxide increased, indicating that richness in bacteria increased, but that no acid fermentation of lactose occurred (this vol., ii, 326) during this period. The increase in catalytic activity of milk varies with the race of lactic bacillus it contains, and is much more marked for milk kept in a dairy than for milk kept in the laboratory. Further, the catalytic activity increased more rapidly in milk kept warm than in milk preserved at about 10°.

T. A. H.

**Estimation of Diastase in Milk.** C. J. KONING (*Chem. Weekblad*, 1910, 7, 377. Compare van Haarst, *Chem. Weekblad*, 1910, 7, 354—355).—A reply to van Haarst's statement that Koning's method for estimating diastase in milk is useless.

A. J. W.

**Estimation of Diastase in Milk.** J. VAN HAARST (*Chem. Weekblad*, 1910, 7, 391).—Polemical. A reply to Koning (preceding abstract).

A. J. W.

**The Apparent Diastase Reaction of Water on Starch.** C. J. KONING (*Chem. Weekblad*, 1910, 7, 484—485. Compare preceding abstracts).—A reply to van Haarst, maintaining that the author's method of estimating diastase in milk is trustworthy.

A. J. W.

**Analysis of Gastric Juice.** ALFREDO E. TAMAYO (*Ann. Chim. anal.*, 1910, 14, 172—173).—*Estimation of Pepsin*.—A solution is made containing 2 grams of pure albumin in 100 c.c. of water, and 0.8 c.c. of hydrochloric acid is added. Ten c.c. of this are added to 10 c.c. of the gastric juice contained in a test-tube; in a similar test-tube are introduced 10 c.c. of the albumin solution and 10 c.c. of water, and both tubes are then placed in a bath at 37° for an hour. The contents of the tubes are then transferred to two Esbach tubes up to the mark *U* and then diluted with dilute nitric acid (20 vol.%) up to the mark *R*. After some time, the volumes of the respective albumin deposits are read off, and the difference represents albumin acted on by the gastric juice.

**Total Acidity and Organic Chlorine.**—To 10 c.c. of the filtered sample are added three or four drops of strong alcoholic solution of phenolphthalein, and *N*/10-sodium hydroxide is added from a burette until a permanent rose colour is noticed. The liquid is then put into a flat porcelain dish and evaporated to dryness. The residue is heated to redness, and, when cold, the ash is moistened with a little water, and a volume of *N*/10-sulphuric acid equal to that of the alkali (*X*) used is added. After boiling to expel carbon dioxide, the excess of acidity is titrated with *N*/10-sodium hydroxide; the number of c.c. (*x*) used represents the hydrochloric acid, *X* - *x* represents the organic acidity. On subtracting from *x* the figure found for free hydrochloric acid, the organic chlorine is found.



*Estimation of Total Chlorine.*—Ten c.c. of the gastric juice are mixed with an excess of sodium carbonate, and, after evaporating to dryness, the residue is ignited. The ash is dissolved in water, and the chlorine titrated as usual.

*Estimation of Free Hydrochloric Acid.*—Ten c.c. of the sample are titrated with  $N/10$ -sodium hydroxide until a drop of the liquid gives no longer the Gunzburg reaction on a warm porcelain slab.

The mineral chlorine is found by deducting from the total chlorine the chlorine existing as free hydrochloric acid and in organic combination.

L. DE K.

*Rapid Detection of Emulsin.* E. FRANKLAND ARMSTRONG (*Proc. physiol. Soc.*, 1910, xxxiii; *J. Physiol.*, 40).—The term emulsin is used for the mixture of enzymes discovered in almonds by Liebig and Wöhler. The material to be tested is incubated with water for twenty-four hours in a corked tube, in the neck of which a piece of moistened Grignard's sodium picrate paper is suspended. As long as the paper remains orange, hydrogen cyanide is absent. A solution of amygdalin, phaseolinnatin, or other cyanophoric glucoside is added, and the tube again incubated. If emulsin is present, hydrogen cyanide is rapidly produced, and the paper becomes coloured red; the speed of the change is a rough measure of the proportion of enzyme present.

W. D. H.

*Is there Caramelisation in Rivas' Test?* DAVID W. HORN (*Ann. J. Pharm.*, 1910, 82, 151—161).—It is contended that the assumption sometimes made that "the development of a brown colour (1) in old official "syrup of ferrous iodide," (2) when lactose is heated with sodium hydroxide, as in Rivas' test for *Bacterium Coli*, is due to the formation of caramel, is inaccurate. It is found that the optical rotation of dextrose is destroyed by heating with alkalis, that the brown colour formed in this reaction disappears on the addition of acids, and that it is also removed by passing oxygen through the solution. In the last respect the brown colour differs from that due to caramel. From information already on record regarding the action of alkalis on dextrose, it appears likely that a sodium dextrose compound is first formed, and that on further heating, organic acids and resin are produced. The lactose in Rivas' test, and the sucrose in the ferrous iodide syrup, may be supposed to break up, yielding dextrose, which might then condense to coloured substances, as described above.

T. A. H.

## General and Physical Chemistry.

**Calculation of Optico-chemical Constants.** H. STANLEY RINGROVE (*Chem. News*, 1910, 102, 3-6, 14-15).—The method already employed in calculating thermochemical constants (compare Abstr., 1907, ii, 446, 604, etc.), in which the influence of the ethane and certain other links usually ignored is taken into account, is now applied to the experimental data for the refractive indices of aliphatic hydrocarbons. The molecular refractivities of these hydrocarbons for the  $\alpha$ - and  $\gamma$ -hydrogen lines, calculated with the help of the "fundamental constants," are tabulated, and are shown to be in good agreement with the experimental values. The observed and calculated molecular dispersions are also in satisfactory agreement, but the results are less trustworthy, as the measurements are greatly affected by experimental errors. It is shown that the molecular dispersion of any hydrocarbon can be calculated by multiplying the number of ethane links in it by 0.13, the number of ethene (double) links by 0.32, and the number of ethine (triple) links by 0.28. The latter constant, however, is somewhat uncertain, owing to the scanty experimental data.

Brühl's method of calculating optico-chemical constants is open to object, a, not only because certain links are not taken into account, but also because his constants are in some cases based on the assumption that aldehydes and ketones contain carbonyl oxygen only, whereas they are often equilibrium mixtures of enolic and ketonic forms.

G. S.

**Production of the Fundamental Spectra of Potassium, Rubidium, and Cesium.** EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1910, 12, 426-443; *Physikal. Zeitsch.*, 1910, 11, 560-568. Compare Abstr., 1907, ii, 725; 1909, ii, 2).—The method described previously for the production of well-developed line spectra of the alkali metals and the halogens has been applied to the examination of alkali-metal fluorides. With suitable condensers placed in parallel with the discharge tube, line spectra of the halogens are obtained in the case of chlorides, bromides, and iodides. Fluorides, however, do not give the corresponding spectrum of fluorine, but under these conditions the so-called "fundamental spectra" of the alkali metals are developed. These spectra are characterised by the fact that the individual lines cannot be represented by any of the usual series formulae. As the intensity of the condenser discharge increases, the series spectrum of potassium is gradually obliterated, and is replaced by the non-series "fundamental spectrum."

"Fundamental spectra" of rubidium and cesium can be obtained in a similar way. As compared with potassium, the only difference exhibited by these metals lies in the fact that the conditions requisite for producing the two independent spectra are not so sharply differentiated in the case of rubidium and cesium.

H. M. D.

**Spectra of Bismuth.** WILHELM SCHWETZ (*Zeitsch. wiss. Photochem.*, 1910, 8, 301—315).—The spark, arc, and flame spectra of bismuth have been examined. From his own and previous observations, the author draws the conclusion that the flame spectrum of metallic bismuth is free from bands, and is characterised principally by the blue line  $\lambda=4722$ . The feebly-developed bands which are observed in the examination of bismuth salts are attributable to bismuth oxide. This band spectrum is also obtained in the case of bismuth chloride.

The spark and arc spectra are contrasted, and observations relating to the influence of pressure, self-induction, and a magnetic field on the spectrum are recorded.

H. M. D.

**Arc Spectrum of Zirconium.** ALBERT BACHEM (*Zeitsch. wiss. Photochem.*, 1910, 8, 316—332).—Detailed measurements have been made of the wave-lengths and relative intensities of the lines in the arc spectrum of zirconium between the limits  $\lambda=2166$  and  $\lambda=7160$ . The wave-length measurements are based on the values of Buisson and Fabry for the normal lines of iron.

H. M. D.

**Connexion between Band Spectrum and Chemical Dissociation.** JOHANN G. KOENIGSBERGER and K. KÜPFERER (*Physikal. Zeitsch.*, 1910, 11, 568—571).—Of the three types of absorption spectra which are exhibited by gaseous substances, the authors attribute the discontinuous band spectrum to intramolecular or intra-atomic conditions which are brought about by the process of chemical dissociation. Substances like iodine, bromine, sulphur, and selenium, the molecules of which undergo dissociation when the temperature is raised, exhibit a discontinuous band spectrum when the conditions are such that both undissociated and dissociated molecules are present in appreciable proportions. If by altering the conditions of temperature and pressure, one set of molecules is caused to disappear more or less completely, the substance in question will no longer give the discontinuous band spectrum.

H. M. D.

**Extreme Red and Infra-red Band Spectra of Carbonated Gases.** F. CROZE (*Compt. rend.*, 1910, 150, 1672—1673).—The spectrum of carbon monoxide consists of fourteen visible bands and a number of ultra-violet bands, the principal lines of which obey Deslandres' law. The author has photographed five bands of the same series in the infra-red, in which the wave-lengths of the headlines are  $722\cdot5$ ,  $747\cdot2$ ,  $792\cdot5$ ,  $836\cdot8$ , and  $881\cdot0\mu$ .

The cyanogen spectrum consists of two series of bands, the first extending from  $4607\mu$  into the ultra-violet, and the second composed, according to Thalen, of thirteen bands between  $7102\mu$  and  $5245\mu$ . This series extends into the infra-red, the headlines of the bands observed being  $725\cdot4$ ,  $740\cdot0$ ,  $753\cdot6$ ,  $800\cdot1$ , and  $813\cdot4\mu$ , whilst beyond these bands a very feeble continuous spectrum appears. An exposure of six to eight hours was necessary, and during this time fresh cyanogen was constantly circulated through the Geissler tube at 2 mm. pressure to prevent the appearance of the nitrogen bands.

Carbonated gases give the above two spectra and also Swan's spectrum, usually attributed to hydrocarbons or carbon. Bergmann has recently mapped the spectrum of the carbon arc between  $640\mu\mu$  and  $1400\mu\mu$ , but the bands grade off in the opposite direction to Swan's. The author has photographed Bergmann's spectrum of the arc directly both in air and in a vacuum.

R. J. C.

The Band Spectrum Obtained by Introduction of Manganese Chloride into the Oxygen Coal-gas Blow-pipe Flame. HERMANN CASARETTO (*Zeitsch. wiss. Photochem.*, 1910, 8, 381—404).—Measurements of the band-spectrum were made between  $\lambda=4402.4$  and  $\lambda=6707.6$ . The photographic records indicate that in this region there are ten similarly constituted groups of bands which fade away towards the red end of the spectrum. It is shown that the frequencies of the constituent bands of the respective groups are related to one another, and that the frequencies of corresponding bands of the several groups show differences which are very nearly constant.

The same band spectrum is obtained with other compounds of manganese, but the bands are more clearly developed in the case of the chloride. This leads the author to infer that the band spectrum is due to the metal itself.

H. M. D.

Conditions Under which the Band Spectrum Attributed to Cyanogen may Appear. ANTOINE DE GRAMONT and DRECO (*Compt. rend.*, 1910, 150, 1235—1236).—The spectrum of sodium carbonate, or of sodium bromide or chloride containing 0.5% of carbon as carbonate, obtained by the use of a spark sufficiently powerful in itself to fuse the salts, showed all the characteristic bands of cyanogen. The salts were free from cyanide, and the conditions such that any cyanogen formed from the carbon and atmospheric nitrogen would be immediately decomposed, since, according to Andrews and Tait, cyanogen is decomposed into its elements by the electric spark. It is suggested that the spectrum usually attributed to cyanogen is merely the spectrum of a mixture of carbon and nitrogen. The bearing of this theorem on the question of the toxicity of Halley's Comet is discussed.

R. J. C.

Three-fold Emission Spectra of Solid Aromatic Compounds. EUGEN GOLDSTEIN (*Brit. Assoc. Rep.*, 1909, 129—131. Compare this vol., ii, 469).—An aromatic substance, when cooled in liquid air and submitted to the action of cathode rays, does not, as was originally supposed (*Abstr.*, 1904, ii, 689, 690), emit only a single spectrum. For each substance there appear three spectra, (a) the *initial spectrum*, (b) the *chief spectrum*, and (c) the *solution spectrum*. The first appears at the moment when the cathode rays fall upon the substance; its brightness diminishes and ultimately becomes very small, but it never entirely disappears. The light belonging to the initial spectra for colourless substances is always blue. The initial spectra begin in the red, but extend through the green and blue into the ultra-violet; for two substances they are similar in general appearance, but never identical. The chief spectrum appears and grows brighter whilst the intensity of the initial spectrum is diminishing. In a large number

cases it is so characteristic that it can be employed as a means of identification, even of isomeric compounds. The chief spectra always begin from the infra-red and end in the green or blue, or in some instances in the yellow.

The solution spectrum, which differs entirely from the others, appears when the aromatic substance is dissolved in a solvent and the solidified solution exposed to cathode rays. Whilst isomeric substances exhibit quite distinct solution spectra, the same substance emits different solution spectra when dissolved in different, even if isomeric, solvents. The light of the chief spectra is fluorescent, but that of the solution spectra is phosphorescent.

E. H.

**Dynamic Isomerism.** HENRY E. ARMSTRONG, THOMAS M. LOWRY, EDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Report*, 1909, 135—141).—This report summarises the evidence showing that the presence or absence of a band in the absorption spectrum of a camphor derivative is independent of the occurrence of isomeric change. The catalytic action of impurities on the phenomena of colour, fluorescence and riboluminescence, and the relation of crystallisation to phosphorescence, fluorescence, and colour, are considered.

E. H.

**Absorption and Fluorescence of Rubidium Vapour.** TAYLOR S. CARTER (*Physikal. Zeitsch.*, 1910, 11, 632—633).—When white light is allowed to fall on the vapour of metallic rubidium, it emits a well-developed, red-coloured, fluorescent beam of rays. Photographic records show that the fluorescence spectrum is discontinuous. The banded absorption spectrum, which determines the nature of the fluorescence, is found to be closely similar to the absorption spectra of potassium and sodium.

H. M. D.

**Magnetic Rotation of the Plane of Polarisation in Crystalline Liquid Substances.** GERHARD VIETH (*Physikal. Zeitsch.*, 1910, 11, 526—527).—Measurements of the rotation of the plane of polarisation by the active amyl anisylideneamino- $\alpha$ -methyleinnamate in a magnetic field have shown that the rotations produced with oppositely directed fields are unequal. For yellow light, the dextro-rotation is about 8.3 times as large as the laevo-rotation; for green light, the ratio of the two rotations is only about 1.75. In all cases the rotation increases in proportion to the intensity of the magnetic field.

H. M. D.

**The Transmission of  $\beta$ -Rays.** J. ARNOLD CROWTHER (*Proc. Camb. Phil. Soc.*, 1910, 15, 442—458).—Experiments were carried out on the velocity and absorption of a beam of  $\beta$ -rays of radium rendered nearly homogeneous by passage through a circular arc in a uniform magnetic field, after the manner employed by W. Wilson (*Proc. Roy. Soc.*, 1909, A, 82, 612), except that a vacuum was employed to avoid the scattering of the rays by air whilst in the magnetic field. It was shown by the use of two similar arrangements, in which the magnetic field of the first was kept constant whilst that of the second was varied, that the velocity of the rays transmitted by a single arrangement did not vary

more than 1% from the mean value. The introduction of an absorbing sheet of aluminium (0.047 cm. thick) between the two arrangements caused a small but decided reduction in the velocity of the rays transmitted [from  $2.735 (\times 10^{10}$  cm./sec.) to 2.690 in one case, and from 2.903 to 2.881 in another]. In the first case, for the softer rays, the screen caused a reduction of 71%, and in the second case of 52% of the radiation, showing that the absorption is not due to any important extent to simple retardation. Glass behaved similarly to aluminium, but platinum was different, the beam, initially homogeneous, emerging with considerable range of velocity in either direction, but particularly in that of retardation. The law of absorption of these homogeneous  $\beta$ -rays was studied for aluminium and platinum. For the former the curve was neither exponential nor linear, but for the latter it was, after a slight initial steeper part, strictly exponential. The latter result is ascribed to the complete conversion of the rays into secondary rays in the first 0.001 cm. of platinum traversed. The analogy between the exponential absorption of these secondary  $\beta$ -rays and of secondary homogeneous  $X$ -rays is pointed out.

F. S.

**Relationships in the Emission of  $\beta$ -Rays and the Absorption of these by Matter.** OTTO HAHN (*Ber. Deut. physikal. Ges.*, 1910, 12, 468—474).—The deviability of  $\beta$ -rays by a magnetic field has been investigated by means of their action on a photographic plate. The photographic record obtained in the case of the  $\beta$ -rays emitted by the active deposit of thorium shows two very distinct bands, corresponding with the emission of two types of  $\beta$ -rays. These are the rays emitted by thorium-A and thorium-D respectively. Three other feebly-developed bands are also recognisable, and it appears therefore that the active deposit of thorium emits five different sets of  $\beta$ -rays.

When examined in the same way, radium-E<sub>2</sub> was found to give homogeneous  $\beta$ -rays. On the other hand, mesothorium-2 appears to emit at least six kinds of  $\beta$ -rays, and the photographic record obtained in the investigation of thorium-X shows that this also emits  $\beta$ -rays.

None of these substances gave a continuous  $\beta$  ray spectrum, and the apparently continuous spectrum obtained by previous observers in the case of radium is attributed to the overlapping of a large number of independent bands.

H. M. D.

**The Structure of  $\gamma$ -Rays.** EDGAR MEYER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 32, 647—662; *Jahrb. Radioaktiv. Elektronik*, 1910, 7, 279—295. Compare von Schweidler, this vol., ii, 376).—If the  $\gamma$ -rays were propagated as spherical waves from their origin, the von Schweidler variation due to the individual atomic disintegrations would not be altered by narrowing the cone of rays under investigation, but on the newer alternative view that the  $\gamma$ -rays are propagated along lines [as discrete particles (Bragg), energy-bundles (Einstein, Stark), or localised in ether-patches (J. J. Thomson)], a second von Schweidler variation of intensity would be superimposed, due to the heterogeneous structure of the "wave-front," and this would come into evidence the more as the pencil of rays is narrowed. The von Schweidler variations with a radium  $\gamma$ -ray source at the centre of a

hemispherical ionisation chamber were observed when the angle of the rays was diminished from  $2\pi$  by lead screens. In several series of experiments the results were in agreement with the second hypothesis, and were incompatible with the first. The relative values of the variation for wide and narrow cones of rays were in good agreement with the results to be expected on the second hypothesis, calculated from the theory as developed by von Schweidler and K. W. F. Kohlrausch. It was proved in separate experiments that the results could not be due to variation of the ionisation of the gas, or of the secondary rays emitted from the walls of the ionisation chamber, for when these factors were varied, the character of the phenomena was not essentially altered. About 30,000 observations were made, and the error is estimated at about 10%, but the conclusion is clearly in favour of the rays being strongly anisotropic in structure, although whether they are propagated along lines or along narrow cones, widening as the distance from the origin is increased, is not apparent from these experiments.

F. S.

**Secondary Röntgen Rays from Metallic Salts.** J. L. GLASSON (*Proc. Camb. Phil. Soc.*, 1910, 15, 437—441).—The question examined was whether the nature of the characteristic homogeneous secondary X-radiation, produced when an element of atomic weight greater than 40 is subjected to X-rays (Barkla), was affected by the state of chemical combination of the element. The results with various salts of iron showed that even when the iron in the molecule is only one-sixth of the whole mass, and is, moreover, in the acid radical (as in ammonium ferrocyanide), the radiation is mainly the homogeneous iron radiation, the light elements producing only a very small proportion of scattered primary radiation, which is considerably more penetrating than the secondary, and so comes into evidence only when the intensity is greatly reduced by absorption screens. The value of the absorption-coefficient for aluminium for the secondary X-radiation characteristic of any metal can be determined quite well by the use of its salts, and for manganese was found to be 100, by using manganese sulphate, which agrees with that predicted from its atomic weight.

F. S.

**The Production of Cathode Particles by Homogeneous Röntgen Radiations.** R. T. BEATTY (*Proc. Camb. Phil. Soc.*, 1910, 15, 416—422).—Radiators of iron, copper, zinc, arsenic, and tin were subjected to primary X-radiation, and the homogeneous secondary X-radiations produced were (1) measured by means of an electroscopa, and (2) received in a second ionisation chamber, through a parchment window covered with silver leaf, in which the air-pressure could be varied. The object was to investigate the absorption-coefficients ( $\lambda$ ) of the cathode radiations produced by the secondary X-radiations, in air and hydrogen. The latter produce an ionisation proportional to the pressure which can be subtracted from the total ionisation, the first was to the cathode radiation (which is independent of pressure). The velocity of the latter is sufficiently high for all the radiation to be absorbed.

can be found; and the absorption-coefficients in the two gases determined. These are given in the following table in cm. units:

	Iron.	Copper.	Zinc.	Arsenic.	Tin.
Air .....	87.2	51.9	42.7	27.43	3.97
Hydrogen.....	17.05	9.55	7.71	—	0.51

It was deduced on various assumptions (1) that the ratio between the energy absorbed by the silver and that used in producing cathode radiation is constant; (2) that the total cathode ionisations in air and hydrogen are the same; (3) that a linear relation holds between the absorption of the generating X-rays in aluminium and that of the generated cathode radiations in air; (4) that the secondary X-rays used produced 175 times more ionisation in air than hydrogen (except tin X-radiation, for which the ratio is 25). F. S.

**French and German Units of Measurement for Radio-active Emanation.** A. JABOIN and G. BEAUDOIN (*J. Pharm. Chim.*, 1910, [vii], 1, 497—499).—The French unit is the quantity of emanation disengaged per minute by 1 mg. of radium bromide in solution, without reference to spontaneous destruction. This unit is independent of the measuring instrument, and remains constant. The German unit is equal to a fall in tension at the electroscope of 1 volt per hour and per litre of radioactive water, and is dependent on the capacity of the measuring instrument. The author has compared the values of the two units by means of the same electroscope, and finds that the French unit is 7000 times as great as the German unit. It is suggested that a common international unit should be adopted.

T. A. H.

**The Atomic Weight of the Radium Emanation.** ANDRÉ DEBIERNE (*Compt. rend.*, 1910, 150, 1740—1743).—A new method is described for the determination of the atomic weight of the radium emanation based on Bunsen's determination of the density from the velocity of escape of a gas through a small hole in a thin partition. The emanation, mixed with varying amounts of foreign gases, was allowed so to escape from a vessel of 45 c.c. capacity, serving also as a McLeod gauge, at a pressure of about 0.01 mm. of mercury into a much larger vessel maintained vacuum by a Gaede pump kept in continuous operation. The pierced diaphragm consisted of a piece of platinum foil, 0.01 mm. thick, and communication could be made or interrupted at will by a wide-bore tap. The pressure in the gauge, with the gas escaping, diminished exponentially with the time over a range from 0.2 to 0.002 mm., and the exponential-coefficient was found to be inversely proportional to the density of the gas for sulphur dioxide, carbon dioxide, oxygen, and argon. For a mixture of oxygen and argon, each gas behaved under the conditions as if alone present at its partial pressure. For the emanation, the amount remaining was determined by means of the penetrating radiation after equilibrium had been attained, and the amount of foreign gas, between the limits of 0.5 and 10 per cent. of emanation, had no effect on the rapidity of escape of the latter. From the exponential-coefficient of escape, the molecular



weight of the radium emanation, as compared with the results for argon and oxygen, was found to be in the neighbourhood of 220. The variations in the separate experiments were not greater than 2 or 3 per cent. This is in remarkable accord with the disintegration theory, from which a molecular weight of 222.5 is to be expected. F. S.

**The Quantitative Measurement of the Radium Emanation.** WILLIAM DUANE and A. LABORDE (*Compt. rend.*, 1910, 150, 1421—1423; *Le Radium*, 1910, 7, 162—164. Compare Abstr., 1905, ii, 219).—The paper deals with the determination of the constants  $C$  and  $K$  in the previously-proposed formula:  $I_0 = C - K.S/V$ , which expresses the initial ionisation,  $I_0$ , due to a given quantity of emanation in a cylinder of length about double the diameter, of interior surface,  $S$ , and volume,  $V$ ,  $C$  being the ionisation that would be produced were all the radiation absorbed in the air. The ratio  $K/C$  had previously been found to be 0.517, so that the above formula may be written:  $I_0 = C(1 - 0.517.S/V)$ . Where  $I_0$  represents the initial current in *E.S.U.* produced by the emanation generated by 1 gram of radium per second,  $C$  has the value 5.19. The volumes of the cylinders varied from 10 to 0.44 litres. The maximum current, produced after three hours, is similarly represented by  $I_{\text{max.}} = 13.15(1 - 0.572.S/V)$ . The results have been checked by means of standards of radium, for which Mme. Curie found the atomic weight 226.5. F. S.

**The Amount of Radium Emanation in the Lower Regions of the Atmosphere and its Variation with the Weather.** JOHN SARTERLY (*Phil. Mag.*, 1910, [vi], 20, 1—36).—A long series of successive daily measurements at Cambridge, England, of the amount of radium emanation in the air, by the method of absorbing the emanation in a known volume of air by means of cocoanut charcoal, have been co-ordinated with the prevailing meteorological conditions. The term radium equivalent signifies the amount of radium which would be in equilibrium with the emanation in one cubic metre of air. The average radium equivalent was 105, the lowest 35, and the highest 350 ( $\times 10^{-12}$  gram). The average number corresponds with 1.7 emanation molecules per c.c. of air. The amount was found to be lowest during cyclones and highest during anticyclones, except where, from a study of the trajectories of the surface air-currents, the air was known to have travelled over the sea or very rapidly over the land, when it was low. It was high when the air had spent much time over land. The number of ions produced per second per c.c. of air by the emanation averages 2.1 (max. 7.0, min. 0.7). The average emanation content found by Eve at Montreal is 6/11 of the amount found at Cambridge. The lowest number of ions produced per second in a closed vessel is 8 (by Wright in a zinc vessel in the open air on the ground near the Toronto Physical Laboratory, while on the frozen surface of the non-radioactive waters of Lake Ontario the number was 4 for the same vessel). Of these 8, 4 therefore are due to the penetrating radiation from the ground, and, since 1 in Canada (or 2 in Cambridge) is due to the radium emanation, the remaining 3 must be ascribed to the radioactivity of the vessel. In the free air, it is estimated that the

penetrating rays produce 1 instead of 4, and the thorium emanation 2 in addition to the 1, or 2, due to the radium emanation, making a total of 4, or 3, ions per c.c. per second. F. S.

**The Solubility of the Radioactive Emanations in Liquids**  
R. W. BOYLE (*Trans. Roy. Soc. Canada*, 1909, [iii], 3, III; 75-80).—Experiments on the bubbling of thorium emanation in similar manner through different liquids showed that, as for the radium emanation petroleum oils are the best absorbers, and then follow in order: ethyl alcohol, sulphuric acid, water. Rising temperature diminishes the absorbing power, and so also do dissolved salts, although in relatively small degree. F. S.

**The Radioactivity of the Rocks of the Transandinian Tunnel.** ARNOLD L. FLETCHER (*Phil. Mag.*, 1910, [vi], 20, 36-45).—Nineteen specimens of rock (mostly varieties of tuff, trachyte, and andesite) taken at levels about 1000 feet from the surface in the transandinian tunnel, from 2.4 to 4.7 km. from the Argentine end, were examined for radium and thorium content by Joly's methods. For the former, the mean value was  $0.79 \times 10^{-12}$  gram of radium per gram (maximum 1.4, minimum 0.3), and for the latter  $0.56 \times 10^{-12}$  gram of thorium per gram (maximum 1.1, minimum 0.0), the ratio of the mean thorium to the mean radium ( $0.71 \times 10^7$ ) being similar to that found by Joly for certain lavas (*Abstr.*, 1909, ii, 848). Thus these rocks are strikingly low in radioactive matter, which may be due to the alterations most of the rocks had undergone, and the removal of soluble radioactive matter by percolating water. The total heat evolved is estimated at  $2.9 \times 10^{-10}$  calorie per hour per gram, in agreement with the fact that no abnormally high degree of temperature was experienced in the tunnel. F. S.

**Non-radioactive Minerals Containing Helium.** ARNALDO PUGNI (*Le Radium*, 1910, 7, 146-149).—With different mixtures of pyrolusite and uranium oxide, 1 gram of which was spread over a surface of 4.55 cm.<sup>2</sup>, the radioactivity could be detected with 0.0001 part of uranium oxide, but not with one-half this proportion. Many minerals of which the radioactivity was too feeble to be detected, for example, castorite, several varieties of tourmaline, and a rose-beryl from Elba, also tourmalines from France, Swaziland, New York, and Madagascar, gave clear indications of the stronger lines of helium when quantities of 1 to 4 grams were heated in a charcoal vacuum. The non-radioactive minerals, however, always contain less helium than the radioactive. In the case of a Madagascar tourmaline, existing in large crystals coloured rose or violet internally with an external fairly sharply defined layer of green colour, the latter possessed a radioactivity and helium-content much greater than the interior portion. For beryls from Elba an inactive rose variety possessed more helium than a green one, which was feebly active. In the beryl from Acworth (New Hampshire) examined by Strutt and found by him not to contain radium, other radioactive substances must be present, for it possesses feeble radioactivity. F. S.

**The Radioactivity of the Spring Water of Mülhausen (Alsace).** WOLF JOHANNES MÜLLER (*Physical. Zeitsch.*, 1910, 11, 545—547).—The spring water of Mülhausen was found to possess a radio-activity of about 8 Mache units by means of the apparatus of Schmidt and Kurz. Such a high activity has so far only been observed for medicinal springs. The activity was proved to be entirely due to dissolved radium emanation, and there is no detectable permanent activity in the water. F. S.

**The Radioactivity of Greek Medicinal Springs.** TELEMACHOS KOMNENOS [with ANASTAS DAMBERGIS and BASIL AEGINITIS] (*Chem. Zentr.*, 1910, i, 1634; from *Pharm. Post*, 1910, 43, 189—190).—The radioactivity of the medicinal springs of Aedipsos, Hypati, Cyllene, Loutraki, and Methana is tabulated in electrostatic units. For some (Cyllene) the activity is remarkably small, while for others (Loutraki, Tombasi) it approaches that of the most radioactive springs known. The activity of the springs is supplemented by analytical and temperature details. F. S.

**The Rays of Potassium.** E. HENRIOT (*Compt. rend.*, 1910, 150, 1750—1751).—The radioactivity of various potassium salts is nearly proportional to the content of potassium, and the small differences may be ascribed to differences in the absorption in the salts themselves, and to the fact that some of them are deliquescent. No difference of radioactivity was caused by variation of the temperature between 14° and 140°. The rays from the sulphate and chloride possess the same penetrating power. No phenomenon, not atomic in character, gives rise to electrons travelling with velocities as great as in the case of the potassium radiation, which must be regarded as specific to the atom of potassium. F. S.

**The Electric Charges Acquired in High Vacua by Insulated Potassium Salts and other Radioactive Substances.** (J. C. McLENNAN (*Trans. Roy. Soc. Canada*, 1909, [iii], 3, 111, 81—99).—A considerable surface, in some cases, of the substances examined was exposed in a high vacuum on insulated trays connected to an electrometer. With polonium the substance acquired a positive charge, indicating that more negative than positive electricity was radiated. The same held true, but the effect was much more marked, with an aluminium tube containing radium, the secondary rays excited by the  $\gamma$ -rays in the aluminium causing the action. With uranium nitrate no indication of any charging effect was obtained until the surface was covered with thin aluminium foil to absorb the positively charged  $\alpha$ -rays, when a positive charge was acquired. Hence the amounts of positive and negative electricity radiated in this case are similar. With potassium chloride and sulphate, using an apparatus set up with extreme care, the acquisition of a feeble positive charge was proved. The effects were small, but showed that potassium emits an excess of negatively charged particles. It has not yet been determined whether any positively charged particles are emitted. F. S.

**Behaviour of Bound Electrons in Solid Substances towards Electromagnetic Radiation.** JOHANN KOENIGSBERGER and K. KILCHLING (*Ann. Physik*, 1910, [iv], 32, 843—867).—A theoretical paper in which the observations recorded previously (Abstr., 1909, ii, 367) are examined from the standpoint of the electronic theory. Various methods of calculating the ratio  $e/m$  from dispersion and adsorption measurements are indicated. H. M. D.

**Electrical and Optical Measurements in the Glow Discharge in Sodium and Potassium Vapour.** GEORG GEHLHOFF and KARL ROTTGARDT (*Ber. Daut. physikal. Ges.*, 1910, 12, 492—505).—The electric discharge through potassium and sodium vapours at higher temperatures is accompanied by complete absorption of the residual gases in the discharge tube. The lower limits of temperature at which this occurs are  $175^{\circ}$  for potassium and  $290^{\circ}$  for sodium. Potential measurements show that the total and the cathode potential differences fall to a minimum at the temperatures at which absorption commences. With an iron cathode, the normal cathode fall of potential in potassium vapour is 80 volts, in sodium vapour about 115 volts.

The emission spectrum of the anodic glow light shows both the principal and secondary series of lines. In the case of potassium, the negative glow light shows the secondary series at low temperatures; above  $230^{\circ}$  the fundamental spectrum is seen together with the secondary lines, and above  $300^{\circ}$  the principal series makes its appearance. In the case of sodium vapour, principal and secondary series are found in the spectrum of the negative glow light at lower temperatures. As the temperature rises, the lines of the secondary series disappear with the exception of that in the green. H. M. D.

**Electrochemistry of Proteins. Dissociation of Potassium Caseinogenate in Solutions of Varying Alkalinity.** T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, 14, 528—568. Compare Abstr., 1908, i, 1027).—The conductivity of potassium hydroxide is at first depressed by the addition of caseinogen, but rises again and attains its original value when the solution is saturated with caseinogen.

The alkalinity of solutions of potassium hydroxide with and without caseinogen was estimated by the hydrogen electrode method. The two solutions were contained in the arms of a U-tube separated by a partition of agar-agar saturated with potassium chloride. The difference in hydroxyl ion concentration, that is, the proportion of unneutralised hydroxide in presence of the caseinogenate, was calculated by Nernst's formula from the potential difference set up. Further, by subtracting the conductivity of uncombined alkali from the total electrolytic conductivity, the conductivity of potassium caseinogenate was obtained.

To promote the dissolution of caseinogen, an excess of alkali was taken, and was afterwards neutralised with hydrogen chloride. The conductivity of potassium caseinogenate is not affected by small quantities of potassium chloride in its solution. Potassium caseinogenate, therefore, does not give the potassium ion, but probably dis-

sociates into complex multivalent ions. The mobility of the potassium ion is about  $61 \times 10^{-6}$  cm. per sec. under unit potential gradient. If the velocity of the caseinogen ion were  $15 \times 10^{-3}$ , the maximum molecular conductivity of potassium caseinogenate would be  $73 \times 10^{-3}$  ohm at  $18^\circ$ . Conductivities ranging from  $80 \times 10^{-3}$  to  $120 \times 10^{-3}$  were observed. As the caseinogen becomes more concentrated its combining capacity for potassium decreases, but the "molecular" conductivity of the caseinogenate increases. Concentration leads to increased complexity of the caseinogen molecule and increased facility for the formation of complex multivalent ions.

The same hypothesis explains why the sum of the apparent velocities of the ions of ammonium caseinogenate is less than the velocity of the ammonium ion alone. The acidity of caseinogen, according to the gas electrode measurements, tends to become proportional to the concentration of alkali at low alkalinities, but approaches a constant maximum in presence of excess of alkali,  $180 \times 10^{-3}$  gram-molecules of hydroxide combining with 1 gram of caseinogen. On precipitation with ammonium sulphate, some of the alkali is eliminated from the caseinogenate.

The potentiometer determinations show that in those solutions containing no free hydroxyl ions, each gram of casein was combined with  $51 \times 10^{-3}$  gram-molecules of potassium hydroxide at  $30^\circ$ . Previous observations by the titration method have given  $50 \times 10^{-3}$  equivalents as the amount of alkali required to produce neutrality to litmus.

The depression in conductivity of a solution of potassium hydroxide at  $30^\circ$ ,  $\lambda \times 10^5 = 26806 - 4758006^2/c - 28.98c$ , where  $\delta$  is the concentration of alkali, and  $c$  the percentage of caseinogen. By extrapolation the conductivity of the alkali would be unaffected ( $\lambda=0$ ) when  $\delta=0.00114c$ . This is actually the ratio between  $\delta$  and  $c$  in solutions which are saturated with caseinogen. R. J. C.

**Absorption of Electrical Waves by Alcohols.** P. BRAULÉD (*Compt. rend.*, 1910, 151, 55—57. Compare Abstr., 1906, ii, 3).—The author has determined the apparent specific inductive capacity,  $\epsilon$ , of glycerol and twelve monohydric alcohols for wave-lengths of 12 and 35 metres, and employed the results to calculate the value of  $\chi$  in the expression  $\epsilon = n^2(1 - \chi^2)$ , using Drude's values for  $n^2$ , the true specific inductive capacity. With the exception of allyl alcohol all the compounds examined showed anomalous dispersion for electrical waves. W. O. W.

**Dielectric Cohesion of Argon.** EDMOND BOUTY (*Compt. rend.*, 1910, 150, 1643—1647. Compare Abstr., 1904, ii, 309).—The critical sparking potential in a given sample of argon at constant pressure is subject to large secular variations, which render the value of the dielectric cohesion somewhat uncertain. If  $y$  is the minimum sparking potential,  $b$  the cohesion, and  $p$  the pressure,  $y = a + bp$ , where  $a$  is a coefficient depending, not only on the gas, but on the nature and condition of the containing surfaces. It is shown that with argon  $a$  may be greatly influenced by the presence of mercury vapour in the pressure gauge, and also by preliminary cooling of the argon in liquid air.

By measuring  $\alpha$  at three different pressures as quickly as possible, values of  $\alpha$  and  $\beta$  were obtained on the assumption that  $\alpha$  did not vary during the time taken by the measurements.

A series of determinations made in this way from time to time gave a constant value, 38, to the dielectric cohesion,  $\beta$ , whilst  $\alpha$  varied from 539 to 659. With argon recently cooled in liquid air,  $\alpha$  is practically zero, but rises in a few days to 800—900.

The value 38 of the cohesion is practically identical with that previously obtained, 39, using argon from another source.

R. J. C.

**Photoelectric Effect Exhibited by Zinc in Hexane.** GEORGE AFFÉ (*Physikal. Zeitsch.*, 1910, 11, 571—575).—Experiments are described which show that zinc, immersed in hexane, has photoelectric properties similar to those exhibited by the metal when surrounded by air. The relative intensities of the photoelectric effect in the two cases depend on the strength of the electric field, on the nature of the incident ultra-violet light, and on the length of time during which the metal has been exposed to the incident rays. In a special case the effect in hexane was found to be about one-thousandth of the corresponding effect in air.

H. M. D.

**Platinum-Rhodium Thermo-element from 0° to 1755°.** OBERT B. JOSMAN (*Amer. J. Sci.*, 1910, [iv], 30, 1—15).—In a previous paper (compare this vol., ii, 261) the *E.M.F.* of the platinum-rhodium thermo-element has been referred to the scale of the nitrogen thermometer between 400° and 1550°, and the comparison, and hence the behaviour of the nitrogen thermometer, is now extended to the m. p. of platinum, 1755°, and also from 0° upwards. The above value for the m. p. of platinum has been further confirmed by extrapolation of the curves of thermo-elements containing 1—15% rhodium, and is probably accurate within 5°. The data for the low temperature-interval are the m. p. and b. p. of water, the b. p. of naphthalene, 217.7°, of benzophenone, 305.4°, and the m. p. of cadmium, 321°. A simple method of interpolating temperatures with the 10% thermo-element is described.

The variation with temperature of the thermal *E.M.F.* of platinum-rhodium alloys has been determined, and is shown graphically. At low temperatures the *E.M.F.* increases very rapidly with the first additions of rhodium, and at 20% the value has already reached within 1% of the *E.M.F.* of platinum against pure rhodium. The rate of variation of the *E.M.F.* with temperature is also plotted against the atomic composition of the alloy. The data indicate that from 20 to 55 atom per cent. of rhodium solid solutions, but no compounds, are formed.

G. S.

**The Lead Coulombmeter.** I. FRANZ FISCHER and KARL HILDE (*Zeitsch. anorg. Chem.*, 1910, 67, 302—316).—The object of the investigation is to determine the most suitable lead salts for use as electrolytes in the lead coulombmeter.

Hydrogen borofluoride, purified by adding a small quantity of lead

carbonate to precipitate sulphuric and hydrofluoric acids, filtering, passing hydrogen sulphide, and passing air through the filtrate, dissolves lead carbonate without becoming turbid. The solution of lead hexafluoride is neutral to Congo-red, but acid to litmus. Crystals are obtained by cooling to  $0^{\circ}$ , or by evaporating in a vacuum, but they are highly deliquescent, and cannot be freed from liquid. They leave a basic residue when re-dissolved in water. Alcohol precipitates a hygroscopic, basic salt.

Lead aluminofluoride is prepared by dissolving aluminium hydroxide in hydrofluoric acid, adding a little lead carbonate, filtering, and saturating the filtrate with lead carbonate. The solution attacks glass.

Lead silicofluoride is prepared in a similar manner, and has not been obtained in a crystalline form. Lead titanofluoride and zirconofluoride have similar properties.

Complex acids containing tin are best prepared by dissolving stannous fluoride or stannic sulphide in hydrofluoric acid. The stannous solution only contains a small proportion of complex acid, most of the tin being present as stannous fluoride. Lead stannofluoride resembles the other salts of the same group.

Ceric hydroxide dissolves in hydrofluoric acid, but the complex acid decomposes slowly, depositing cerous fluoride. Lead tetra-acetate and hydrofluoric acid also yield an unstable complex acid, which only dissolves a small quantity of lead carbonate. Vanadium yields a complex acid, which only dissolves small quantities of lead.

Arsenic and antimony trisulphides only form small quantities of complex acids when dissolved in hydrofluoric acid, but arsenic and antimony pentasulphides yield solutions which dissolve lead carbonate, although only a part of the salts is present in the complex form. Bismuth peroxide dissolves in hydrofluoric acid at  $-10^{\circ}$ , but the product decomposes when the temperature rises. It was not found possible to compare complex fluorides containing thallium, thorium, or phosphorus.

When the lead salts are electrolysed, lead is deposited quantitatively from the borofluoride and silicofluoride, and probably, under suitable conditions, from the titanofluoride and zirconofluoride; antimony and arsenic are partly deposited with lead, and the deposition from other solutions is not quantitative.

Tin and antimony may be separated by oxidising the solution, passing hydrogen sulphide, and dissolving the precipitate in hydrofluoric acid. Hydrogen sulphide then precipitates only the antimony from the solution. The tin is recovered after decomposing the complex fluoride with sulphuric acid in a platinum basin. Ammonium fluoride may also be used for the extraction of the mixed sulphides, but with less advantage.

C. H. D.

**The Lead Coulombmeter.** II. FRANZ FISCHER, KARL THIELE, and EDWARD B. MAXTED (*Zeitsch. anorg. Chem.*, 1910, 67, 339—356. Compare preceding abstract).—One copper and two lead coulombmeters are connected together in series. The lead anodes are plates  $6 \times 4$  cm. in size, and the cathodes are of platinised platinum foil,  $6 \times 6$  cm. and

0.03 mm. thick, the distance between anode and cathode being 1.5 cm. Copper foil, freshly coated with copper, is used as cathode in the copper cell.

After an experiment, the platinum carrying the deposit of lead is rapidly washed, then lowered into a vessel containing alcohol, and dried in a vertical position in a vacuum desiccator.

For the analysis of the electrolyte, an excess of  $N/10$ -chromic acid solution is added, the precipitate of lead chromate filtered off, and the excess of chromic acid estimated by means of potassium iodide and sodium thiosulphate. When lead phenol-*p*-sulphonate is used, this method is inapplicable, and the lead is estimated gravimetrically. The acidity of the electrolyte is estimated by precipitating the lead with a known excess of sulphuric acid, filtering, and titrating the filtrate with alkali.

Experiments have been made with lead borofluorides, silicofluoride, and phenol-*p*-sulphonate. Too high a proportion of free acid leads to the liberation of hydrogen and the formation of lead sponge, and too low a proportion to crystallisation of the lead. The concentration should increase with the current density, and gentle warming increases the density of the deposit.

A solution of lead borofluoride containing 150 grams of lead and the same weight of free acid per litre gives good results, and may be used for current densities of 0.14–14.0 amperes per sq. dm. A solution of lead silicofluoride of the same, or of lead phenol-*p*-sulphonate of one-half this, concentration also gives good results for ranges of 0.14–11.0 and 0.14–4.9 amperes per sq. dm. respectively. The addition of 0.1–1 gram of gelatin or agar-agar prevents crystallisation, and does not interfere with the accuracy of the determination. C. H. D.

**The Theory of the Determination of Transference Numbers by the Method of Moving Boundaries.** GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1910, 32, 862–869).—In the case of certain solutions, for example, the normal solutions of sodium and potassium chlorides, the transference numbers of the ions have been determined by three methods, namely: (1) the Hittorf method; (2) the method of moving boundaries, and (3) Nernst's method, which gives the "true transference number," and depends on the use of some reference substance in solution which does not wander with the current, and with respect to which rather than to the water the salt content at each electrode is determined. The close agreement obtained by methods (2) and (3) has led Washburn (*Abstr.*, 1908, ii, 1009) and Denison (*this vol.*, ii, 15) to draw the conclusion that the method of moving boundaries gives immediately the true transference numbers. The author shows, however, that this agreement is entirely accidental, and due to the neglect of a correction which must always be made when the method of moving boundaries is employed. This correction is due to volume changes at the electrodes brought about by the disappearance of salt from, or the entrance of salt into, the solution; it is the larger the more concentrated the solution. When this correction is applied, the method of moving boundaries gives,



theoretically and practically, the Hittorf transference numbers, and of the true transference numbers.

The theory of a suggested method for obtaining true transference numbers from moving boundary experiments by the aid of a non-electrolyte which does not migrate with the current is given, but the method still remains to be worked out practically. T. S. P.

**Electrolytic Conductivity of Non-aqueous Solutions at Low Temperatures.** PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1910, 73, 257—268. Compare Abstr., 1904, ii, 227; 1906, ii, 149, 335; 1907, ii, 231, 734).—Kohlrausch (*Proc. Roy. Soc.*, 1903, 71, 338) has shown that the temperature-coefficient of the conductivity  $\alpha$  of aqueous solutions approximates to the temperature-coefficient of the fluidity of water, and the author (*loc. cit.*) has found that the same relationship is approximately valid for organic solvents. In the equation  $K_t = K_0(1 + \alpha t)$ ,  $K_t$ , the specific conductivity at the temperature  $t$ , must become zero at the temperature  $t_x = -1/\alpha$ , provided that the relationship in question holds for low temperatures.

To test this point, the conductivity of tetraethylammonium iodide or the corresponding propyl compound has been determined in twelve organic solvents through a wide range of temperature, in some cases from  $-100^\circ$  upwards. The results show that in no case does the temperature-conductivity curve intersect the temperature axis at an acute angle, as required by the above considerations, but approaches it asymptotically, so that the calculated values of  $t_x$  for the different solvents have no definite physical meaning. In the course of the experiments, the freezing points of the following substances have been re-determined: ethylene glycol,  $-11.2^\circ$ ; furfuraldehyde,  $-36.5^\circ$ ; anisaldehyde,  $-2.1^\circ$ ; methyl cyanoacetate,  $-22.5^\circ$ ; phenylacetonitrils,  $-26.5^\circ$ ; methyl thiocyanate,  $-51^\circ$ , and nitromethane,  $-26.5^\circ$ .

G. S.

**Formamide as a Solvent for Inorganic Salts and the Electrolysis of Such Solutions.** HERMANN RÖHLER (*Zeitsch. Elektrochem.*, 1910, 16, 419—436).—The specific volume of pure formamide between  $-7^\circ$  and  $+25^\circ$  is given very exactly by  $V = 0.8674(1 + 0.000644t)$ . There is no maximum between these limits. The purest material obtained had m. p.  $1.58^\circ$ , and specific conductivity,  $18.9 \times 10^{-6}$ .

Anhydrous copper sulphate dissolves in formamide, yielding a dark blue solution, which soon deposits a light blue, crystalline cupric formamide of the composition  $(\text{H} \cdot \text{CO} \cdot \text{NH})_2\text{Cu} + 2\text{H} \cdot \text{CO} \cdot \text{NH}_2$ . By prolonged heating at  $95^\circ$ , two molecules of formamide are driven off, leaving copper formamide,  $(\text{H} \cdot \text{CO} \cdot \text{NH})_2\text{Cu}$ . The sulphuric acid produced remains dissolved (partly in combination with formamide), and its accumulation limits the reaction. The acid solution, with 0.8% of copper, was electrolysed, using a copper anode and a rotating cathode. The quantity of copper deposited was much less, and that dissolved much greater, than the theoretical amount. It was found that copper reduces the cupric salt to cuprous salt, and also that formamide alone dissolves copper in presence of oxygen. By shaking

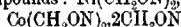
the cupric solution with copper until reduction was complete, and then carrying out the electrolysis in an atmosphere of hydrogen, equal quantities of copper were dissolved and deposited. At 25°, only 29% of the cupric salt is reduced by metallic copper, and the quantity of copper deposited when the solution is electrolysed is about 4/3 of that deposited simultaneously in a copper voltameter.

A saturated solution of cuprous chloride in formamide is colourless, and contains 1.3% of copper; when electrolysed in an atmosphere of hydrogen, the copper dissolves, and is deposited quantitatively in the univalent form. With both the sulphate and chloride solutions the deposits are powdery at first, but improve with continued use of the solution. Lustrous, adherent deposits are obtained with about 0.2 to 0.25 ampere per 100 sq. cms.

Salts of mercury and silver are reduced to metal by formamide; this is also the case with the copper solutions when they are warmed.

Cupric chloride and formamide react in the same way as the sulphate. The hydrochloric acid formed combines with formamide to a colourless, crystalline substance,  $\text{H} \cdot \text{CO} \cdot \text{NH}_2 \cdot 3\text{HCl}$ . The solutions of this substance in formamide conduct electricity well, and dissolve zinc with evolution of hydrogen.

The chlorides of nickel and cobalt react readily with formamide, yielding crystalline compounds:  $\text{Ni}(\text{CH}_2\text{ON})_2 \cdot 2\text{CH}_3\text{ON}$  and



respectively. Like the copper compound, these decompose when heated, leaving a residue of pure metal.

Lead nitrate gives the compound  $\text{Pb}(\text{CH}_2\text{ON})_2$ , but lead chloride takes up a molecule of formamide without decomposition, yielding the substance  $\text{PbCl}_2 \cdot \text{CH}_3\text{ON}$ . Lead formamide decomposes at 200°, leaving metallic lead.

Stannous chloride is very freely soluble in formamide, and reacts with it, but the compound could not be isolated.

Zinc chloride dissolves readily, and the strong solutions deposit zinc formamide,  $\text{Zn}(\text{CH}_2\text{ON})_2 \cdot 2\text{CH}_3\text{ON}$ ; when heated at 100°, this decomposes, losing formamide and water and leaving zinc cyanide.

The metallic formamides are all sparingly soluble in formamide; the solubilities lie between 0.2*N* and 0.005*N* at 25°. The conductivity of the solutions is small.

Solutions of lead chloride (4% of lead), lead nitrate (31.5% of lead), zinc chloride (8.2% of zinc), zinc oxide (0.8% of zinc), and of stannous chloride (14.3% of tin) were electrolysed in the same way as the copper solutions. In each case, compact, adherent deposits were obtained under almost the same conditions described for copper, and, except that no reduction occurs, the results were very similar.

No metallic deposit was obtained when solutions of nickel, cobalt, iron, aluminium, and magnesium salts were electrolysed. T. E.

**Electrolysis of Glass.** ADOLF HEYDWEILLER and F. KOPFERMANN (*Ann. Physik*, 1910, [iv], 32, 739—748).—Experiments are described which show that sodium, potassium, barium, strontium, tin, lead, copper, iron, cobalt, and silver are capable of passing through glass at temperatures of 250—450° under the influence of an electric field.

Negative results were obtained with gold, platinum, and uranium. The glass diaphragm, in the form of a tube, the thickness of which varied from one to two millimetres, was immersed in a molten salt of the metal under investigation, and this served as the anode liquid. The cathode liquid, consisting usually of a mixture of sodium and potassium nitrates, was placed in the tube itself. Similar results were obtained with an easily fusible sodium glass and a much less readily fusible potassium glass.

In many cases the entry of the foreign metal ions into the glass is accompanied by the appearance of pronounced colour effects. These are attributed to the colloidal condition of the metals, and this view is consistent with the appearance of the glass under the ultra-microscope. In general, the conductivity of the glass varies as the electrolysis proceeds, and this is supposed to be due to differences in the mobilities of the various ions.

Similar diffusion phenomena are observed without an electric current, but the process in these circumstances is comparatively slow.

H. M. D.

**Magnetisation of Certain Alloys as a Function of the Composition and the Temperature.** KOTARŌ HONDA (*Ann. Physik*, 1910, [iv], 32, 1003—1026).—The dependence of the magnetic properties of binary alloys on the composition and on the temperature has been examined. Data were obtained for the following pairs of metals: nickel-chromium, cobalt-chromium, iron-vanadium, nickel-tin, nickel-aluminium, manganese-antimony, and manganese-tin. From a comparison of the magnetic data with observations relating to the structure of the alloys, it is found that the ferro-magnetic properties are determined by particular crystalline constituents of the alloys. This is also true in the case of the remanent magnetism. H. M. D.

**Thermo-magnetic Properties of the Elements.** KOTARŌ HONDA (*Ann. Physik*, 1910, [iv], 32, 1027—1063).—The magnetic susceptibility of a large number of elements has been determined at the ordinary and at higher temperatures. A comparison of the data for the ordinary temperature shows that the magnetic susceptibility varies with the atomic weight in a periodic manner. Elements belonging to the same group occupy in many cases corresponding positions on the periodic curve. In respect of the influence of temperature on the magnetic susceptibility, the various elements are tabulated according to whether the susceptibility increases, decreases, or remains practically constant as the temperature rises. H. M. D.

**A Graphic Method for the Correction of Gas Volumes.** ROBERT CROSBIE FARMER (*Analyst*, 1910, 35, 308—309).—A convenient device for the reduction of gas volumes to normal temperature and pressure, the various scales being so arranged that, by means of a rule placed at the points corresponding with the observed temperature and pressure, the corrected volume of 1 c.c. of gas at normal temperature and pressure can be read off. For nitrogen estimations a scale has been added by which the logarithm of the weight of 1 c.c. of nitrogen can be read.

L. DE K.

**Gaseous Explosions.** SIR WILLIAM H. PREECE, DUGALD CLERK, BERTRAM HOPKINSON, WILLIAM A. BONE, BURSTALL, HUGH L. CALLENDAR, ERNEST G. COKER, W. E. DALBY, HAROLD B. DIXON, RICHARD T. GLAZEBROOK, H. S. HELE-SHAW, J. E. PETAVEL, ARTHUR SMITHELLS, W. WATSON, JOHN A. HARKER, H. C. L. HOLDEN, and H. R. SANKEY (*Brit. Assoc. Report*, 1909, 247—270).—This report deals with the measurement of the specific heat of gases at high temperatures, radiation in gaseous explosions, the measurement of temperature, and Deville's experiments on the dissociation of gases.

E. H.

**Thermodynamics of *iso*Pentane.** GÜNTHER VOGEL (*Zeitsch. physikal. Chem.*, 1910, 73, 429—480).—As a preliminary to the discussion of the characteristic equation for *isopentane*, the experimental data of Young for this substance have been supplemented by direct determinations of certain thermal constants. The heat of vaporisation is  $6397 \pm 19.88$  cal. per mol.; the specific heat of the vapour at constant pressure is  $0.4593$  at  $58^\circ$  and  $0.4881$  at  $100.75^\circ$ , and the specific heat of liquid *isopentane* determined by comparison with benzene is  $0.5266 \pm 0.00106$  at  $8^\circ$ .

On the basis of the characteristic equation of Reinganum (*Diss.*, Göttingen, 1899), which is a modified form of van der Waals' equation, the equation  $a = \left( T \frac{\delta p}{\delta T} - p \right) v^2 = \left[ a + \beta + \gamma \frac{\rho_0 - \rho}{1 + c\rho^3} \right] e^{-T/T^1}$ , where  $\rho = 1/v$ , and  $a, \beta, \gamma, c, k^1$  are constants, is deduced, and is shown to represent satisfactorily the thermal behaviour of *isopentane*. From this expression by integration the somewhat complicated characteristic equation for *isopentane* is obtained.

Finally, the above expression  $a = [T(\delta p/\delta T) - p]v^2$  is shown to hold also for ethylene, ethyl ether, and carbon dioxide, and it is probable that the behaviour of these substances could also be represented by characteristic equations similar to that deduced for *isopentane*.

G. S.

**Method for Determining Boiling Points under Constant Conditions.** ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, 30, 432—435).—The apparatus consists of a small bulb with a bent capillary not less than 1 mm. in diameter. The bulb is charged with  $0.03$ — $0.1$  gram of the substance of which the boiling point is to be determined, and attached to a thermometer suspended in a beaker containing the heating liquid, so that the opening of the capillary points downwards. When the temperature of the bath has remained at the boiling point of the substance in the bulb for a few moments, dissolved and occluded gases and moisture have all been expelled, and a rapid stream of pure vapour issues. With falling temperature and vigorous stirring, the point at which the bubbles suddenly cease can be read accurately; this is the boiling point (compare Abstr., 1909, ii, 20). When the substance is soluble in the bath-liquid, the point at which boiling ceases cannot be ascertained sharply. The bath-liquid is then allowed to recede into the

capillary to a fixed point 5—10 mm. from the opening; the temperature at which this point is reached is the boiling point.

Besides the ordinary correction for barometric pressure, a correction must be made for the head of liquid above the opening of the capillary or above the mark to which the bath-liquid ascends. This depth is measured to within 2 mm., and the density of the bath-liquid may be obtained from the following formulæ: Sulphuric acid (92.75%);  $D = 1.818 - 0.000906(t - 30^\circ)$ . Melted paraffin (m. p.  $53^\circ$ );  $D = 0.778 - 0.000612(t - 60^\circ)$ . Mixture of sodium and potassium nitrates (45.5:54.5 parts);  $D = 1.968 - 0.00075(t - 230^\circ)$ .

The method is accurate, and may be applied to non-fusing solids, such as calomel and ammonium carbonate.

T. S. P.

**A Common Thermometric Error in the Determination of Boiling Points under Reduced Pressure.** ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, 30, 436).—When the bulb of a thermometer is enclosed in an evacuated vessel, the dilatation of the bulb introduces a considerable error into the temperature readings. In the case of some thermometers which were tested, a diminution in pressure from 748 to 20 mm. caused an error of  $0.10$ — $0.17^\circ$ . This source of error has hitherto not been taken into account in measuring boiling points under diminished pressure.

T. S. P.

**Simple Dynamic Method for Determining Vapour Pressures.** ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, 30, 437—438).—The bulb apparatus described in a previous abstract is used. The lower part of the thermometer is enclosed in a test-tube containing a portion of the bath-liquid. The interior of the test-tube communicates, through a right-angled tube inserted in the cork, with a pump and with the atmosphere. The bath is brought to constancy at the required temperature with the pressure in the apparatus above the vapour pressure of the substance. The pressure is next lowered gradually until a continuous stream of bubbles issues from the capillary. Then the pressure is allowed to rise until the stream just ceases, which gives the vapour pressure at the temperature of the bath.

T. S. P.

**Vapour Pressure of Water and Aqueous Solutions of Sodium Chloride, Potassium Chloride, and Sucrose.** FRANCIS C. KRAUSKOPF (*J. Physical Chem.*, 1910, 14, 489—508).—The water contained in a known volume of air saturated at the vapour pressure of each solution was estimated by direct weighing in absorption tubes. From 2 to 28 litres of air were drawn over the solution in about one hour, the volume being so chosen as to give about 1 gram of water in each case. The method and apparatus used were described by Lincoln and Klein (*Abstr.*, 1907, ii, 435), with the difference that heavy gas-engine oil with practically no vapour pressure was used in the aspirator instead of water.

The vapour pressures of water at various temperatures are as follows:  $25^\circ$ , 23.71 mm.;  $30^\circ$ , 31.84 mm.;  $35^\circ$ , 41.91 mm.;  $40^\circ$ ,

55.18 mm.; 50°, 92.16 mm.; 60°, 149.26 mm.; 70°, 233.99 mm.; 80°, 355.08 mm. These values are in good agreement with previous observations.

The vapour pressures of sodium chloride and potassium chloride solutions at 40° and 60° show an apparent increase in molecular weight as the solutions become more dilute. This agrees with Kahlenberg's freezing-point and boiling-point determinations, and is opposed to the dissociation theory.

The molecular weight of eucrose appears to decrease with increase in the dilution.

R. J. C.

**Vaporisation. V. HANNS VON JÜPTNER** (*Zeitsch. physikal. Chem.*, 1910, 73, 343—382. Compare Abstr., 1908, ii, 663, 810; 1909, ii, 21; this vol., ii, 583).—It is suggested that the deviations from van der Waals' equation are connected with the simultaneous existence of liquid and vapour, and that the equation is strictly valid for a single phase (liquid or vapour). A number of relationships are deduced for "ideal" conditions, that is, when only one phase is present.

For ideal liquids the ideal density is proportional to the temperature. At the absolute zero it is four times the critical density, and is zero at  $T''_k = 2T_k$ . The temperature  $T''_k$  is therefore called the absolute critical point.

$T_k = 3/2T''_k$  is the ideal critical point; at this temperature the ideal density of the liquid is equal to the critical density, and, further,  $\pi_k = 3p'_k$ ,  $v'_k = 3b'_k$ , and  $v/v_k = 8/3$ , where the symbols have the usual significance and ideal conditions are indicated by the ' sign.

The surface-tension of the ideal liquid is represented by the formula  $\pi_k/\pi_k = a(D/D_k)^2 = 4$ , and is diminished in the presence of vapour (owing to the capillary attraction of the vapour molecules) to  $\pi_k/\pi_k = a(4-1) = 3a$ . As the internal pressure is thus reduced, the liquid expands.

If the vapour density is represented by  $d$ , the ideal liquid density by  $D$ , the relationships hold:  $\pi_d = ad^2$ ,  $\pi_l = aD_l^2$ , and  $\pi_l - \pi_d = a(D_l^2 - d^2)$ . When allowance is made for the diminution of the internal pressure,  $\pi$ , of the liquid, the final value of the latter is  $a(D-d)^2$ . Further, for the ideal liquid the following relationships hold:  $D/D_k = 4 - 2\theta$ ;  $v/v_k = 1/(4 - 2\theta)$ , and  $\pi/\pi_k = (4 - 2\theta)^2$  (for meaning of symbols see *loc. cit.*). The above considerations also afford a simple explanation of the law of Cailletet and Mathias, as the density of the ideal liquid in the presence of its vapour is diminished by the density of the vapour.

For further deductions and illustrations the original paper should be consulted. In particular, the relationship  $p_k v_k/T_k = \text{const.}$  is deduced, and it is shown from the data for over forty liquids that the deviations from the mean value are extremely small.

G. S.

**Crystallisation Temperatures of Binary Mixtures. ÉMILE BAUD and L. GAY** (*Compt. rend.*, 1910, 150, 1687—1690. Compare this vol., ii, 268).—A liquid  $A$  solidifies at  $T$ , where the vapour-tensions of its liquid phase ( $l$ ) and solid phase ( $s$ ) become equal. If a second liquid  $B$  is added to  $A$ ,  $s$  remains unchanged, but  $l$  becomes a partial pressure. Partial pressure is proportional to concentration if the liquids do not interact (compare Dolezalek, Abstr., 1909, ii, 22).

Clapeyron's equation gives for the pure liquid  $A$ ,  $d \log l/dT = EL/RT^2$  and  $d \log s/dT = ES/RT^2$ , where  $L$  and  $S$  are the latent heats of vaporisation of pure liquid and pure solid  $A$ . Hence  $d \log \frac{s}{l}/dT = E(S-L)/RT^2 = EQ/RT^2$ , where  $Q$  is the latent heat of fusion of  $A$ . If now it be assumed that  $Q$  is independent of temperature,  $\Delta t = -K \log x/T_2$ , where  $x$  is the concentration of the component  $A$  in the mixture depositing pure  $A$  at an absolute temperature  $T_2$ . The depression of the freezing point is proportional to the logarithm of the molecular concentration of the solvent, and to the absolute freezing point. In very dilute solutions this expression is identical with Raoult's law.

The authors have verified this equation for mixtures of ethylene dihydride with benzene, toluene, and ether, and of ethylene dichloride with benzene. It is claimed that the assumption that  $(S-L)$  is independent of temperature is justified by the concordance of the results and the equation. This is also to be taken as evidence that the above liquids are non-associated and do not combine.

R. J. C.

**Heat of Solidification of Alloys of Lead and Tin.** DOMENICO MAZZOTTO (*Nuovo Cim.*, 1910, [v], 19, i, 215—232. Compare Guertler, this vol., ii, 126).—The author has repeated his experiments made in 1886 on the heats of solidification of tin and of tin-lead alloys, the method adopted being a comparison of the time of cooling of a crucible containing the tin or alloy with that of a crucible containing an equal volume of mercury. The method of calculation does not involve any hypothesis as to the constitution of the alloy, so that Guertler's objection is disposed of. Two sets of experiments have been made, one with the surrounding medium at  $15^\circ$ , and the other with the medium at  $100^\circ$ ; the results obtained in the two series agree as well as can be expected. In confirmation of his former results, the author finds that there is a well-marked decrease in the heat of solidification in passing from tin to its alloys with lead, the diminution being nearly proportional to the concentration of lead in the alloy, and he can obtain no indication of the increase which can be deduced from Spring's experiments (Guertler, *loc. cit.*). In the author's opinion the cause of the discrepancy lies in the indirect nature of the calculation by means of which the heats of fusion are obtained from Spring's results, the method being such as to magnify any experimental errors. It is pointed out that the results of Guertler are not independent of those of Spring, but are obtained merely by another mode of calculation.

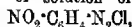
R. V. S.

**Friction in the Bomb Calorimeter.** H. A. ROESLER (*Amer. Chem. J.*, 1910, 44, 80—84).—The heating effect due to the friction of the stirrer in the bomb calorimeter is calculated from the equation:

$F = S_1 - \frac{(S_1 - S_2)}{t_1 - t_2} t$ , where  $F$  is the rate of rise of temperature due to friction, and  $S_1$  and  $S_2$  are the rates of rise of temperature due to radiation plus friction at the temperatures  $t_1$  and  $t_2$ . The value of  $F$  is most accurately determined when one value of  $t$  is nearly zero and the other several degrees above or below. An alternating current.

induction fan motor is the best motive power, since it produces the uniform stirring which experience shows to be necessary to give a constant value of  $F$ . C. S.

**Thermochemical Studies. III. Diazo- and Azo-compounds.** W. STENTOGLAVSKY (*Ber.*, 1910, 43, 1767—1773. Compare this vol., ii, 588).—Thermochemical data are given for the diazotisation of *p*-nitroaniline in aqueous solution, +18.89 Cal., and in acetic acid solution, +18.42 Cal. The heat of solution of the diazonium chloride,



in water is -3.0 Cal. The heat of isomerisation of the diazo-compound into the isodiazo-compound in presence of sodium hydroxide is +13.22 Cal., that is,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2\text{Cl} + \text{H}_2\text{O} = \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{OH} + \text{HCl} - 0.48 \text{ Cal.}$  The heat of solution of *p*-nitroaniline in acetic acid is -4.47 Cal., that of the coupling with  $\beta$ -naphthol, +26.21 Cal., making a total of 40.16 Cal. for the heat of formation of the azo-dye. This value differs largely from that found for other azo-dyes.

E. F. A.

**The Heat of Hydration and Vapour Pressure of the Hydrates of Thorium Sulphate.** IWAN KOPPEL (*Zeitsch. anorg. Chem.*, 1910, 87, 293—301).—The direct measurement of the vapour-pressure of the octa- and tetra-hydrates of thorium sulphate is impracticable, on account of the slowness with which equilibrium is attained. The heat of transformation of one hydrate into the other is also not directly measurable for the same reason, but it may be determined by measuring the difference between the heats of solution. As the solubility in water is very small, it is better to measure the heat of solution in solutions of alkali oxalates or carbonates, the complexity of the reaction being unimportant, as only the difference is required.

A glass calorimeter holding 650 c.c. is used, enclosed in a silvered vacuum vessel, the solvent being 600 c.c. of a 13.32% solution of potassium carbonate. The hydrate is enclosed in a thin glass bulb, which is broken after the temperature has become constant. The heats of solution thus obtained for the octa- and tetra-hydrates respectively are 14944 cal. and 28467 cal., giving the value 13523 cal. for the reaction:  $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} + 4\text{H}_2\text{O} = \text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ . The application of Raoult's formula gives 14424 cal., the vapour-pressures used being calculated from those of the acids with which these hydrates are in equilibrium at the transformation point (compare this vol., ii, 717). Small errors in the vapour pressure, however, give rise to large errors in the heat of transformation.

Using Roozeboom's data for the solubility of the hydrates of thorium sulphate, values for the heat of hydration approximately agreeing with that given above are obtained. C. H. D.

**Cause of Disagreement among the Various Methods of Calculating the Deviations from Avogadro's Law.** PHILIPPE A. GUYE (*J. Chim. phys.*, 1910, 8, 222—227).—The recent work of Gray and Burt (*Trans.*, 1909, 95, 1633) and of Scheuer (*Abstr.*, 1909, ii, 991) gave very concordant values for the density of hydrogen chloride. The atomic weight of chlorine calculated from them varies considerably



according as the corrections of van der Waals' equation are obtained from the compressibility or the critical constants of hydrogen chloride. Comparison with the chemical determinations of the atomic weight of chlorine confirms the figure obtained by use of compressibility data, and suggests that the correction  $(1+a)(1-b)$  from the critical data is too great. This should be the case if hydrogen chloride is associated at its critical point. The same considerations applied to the work of Ter Gazarian (Abstr., 1909, ii, 568) indicate that hydrogen phosphide is associated at its critical point.

According to McIntosh and Steele, liquid hydrogen chloride has the association factor 1.5, and liquid phosphine 1.4, whereas hydrogen bromide, iodide, sulphide, and other permanent gases are not associated. This is held to confirm the author's view.

R. J. C.

**Condensation of Water by Electrolytes.** FRANK K. CAMERON and WILLIAM O. ROBINSON (*J. Physical Chem.*, 1910, 14, 569—575).—The "hydration values" arrived at in a previous paper (this vol., ii, 188) have been found to be generally miscalculated, and also partly founded on incorrect densities. The authors here publish the same tables recalculated, but remark that if the solutes are actually hydrated as their figures indicate, it seems altogether improbable that the density of the dissolved solute is the same as for the solid state; consequently the calculations are meaningless.

R. J. C.

**Adsorption of Certain Dyes.** Léo VIGNON (*Compt. rend.*, 1910, 151, 72—75. Compare this vol., ii, 272, 273).—Solutions of various dyes were passed through asbestos and sand, and the amount of adsorption approximately determined. Adsorption was found to occur with equal readiness whether the substance existed in true or colloidal solutions.

W. O. W.

**Importance of Adsorption for the Precipitation of Suspension Colloids.** HERBERT FREUNDLICH (*Zeitsch. physikal. Chem.*, 1910, 73, 385—423).—The adsorption of the cations of the metallic salts, ammonium chloride, ammonium sulphate, uranyl nitrate, aluminium sulphate, cerium nitrate, and of the following salts of organic bases, aniline hydrochloride, *p*-chloroaniline hydrochloride, morphine hydrochloride, strychnine nitrate, and new-magenta by arsenious sulphide has been determined. As the degree of adsorption is comparatively small and the sulphide could not be obtained absolutely pure, no high degree of accuracy is claimed for the results. The relative activities of the same salts in bringing about the separation of arsenious sulphide from colloidal solution have also been measured.

As far as the organic cations are concerned, those which are most strongly adsorbed are also most active in coagulating arsenious sulphide solutions. On the other hand, the metallic salts investigated, when referred to equimolar concentrations, are adsorbed to about the same extent, and the nature of the anion has very little influence. By means of experiments with uranyl nitrate, cerium nitrate, and the hydrochlorides of aniline and morphine, the general rule has been confirmed that in the coagulation of arsenious sulphide equivalent (not equimolar) amounts of the cations are adsorbed. The coagulation

results with strychnine nitrate proved to be somewhat irregular. Experiments on the coagulation of solutions of colloidal gold confirm the results of previous observers.

The above results are regarded as supporting the adsorption theory of the coagulation of colloidal solutions by electrolytes. The fact that cations of different valency are adsorbed in equimolar proportions is in harmony with the experimental fact that their coagulating powers (which correspond in the first instance with equivalent amounts) are very different. Instead of comparing the relative quantities of different substances required to bring about coagulation, it is preferable for purposes of calculation to subtract from these amounts the quantities adsorbed. G. S.

**The Use of Chitin in Dialysis.** CARL L. ALSBERG (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xii).—Excellent dialysers may be made from the lobster's claw, freed from protein, calcareous salts, and acid. It has great strength. Large sheets of chitin can be obtained from the carapace of the horse-shoe crab. There is some evidence that chitin exerts a selective action, but this is still under investigation. W. D. H.

**Osmotic Phenomena.** WENDELL G. WILCOX (*J. Physical Chem.*, 1910, 14, 576—595).—The author has measured the osmotic pressures, relative to rubber membranes, of dilute pyridine solutions of sucrose, silver nitrate, and lithium chloride. If osmosis is, as Kahlenberg suggested, a distribution phenomenon in which the solution and the membrane compete for the solvent, it should be possible to make a solution of small but finite dilution, such that the membrane would not give up solvent to it and no osmotic pressure would be developed.

The pyridine used was purified from picolines and water by oxidation with permanganate, followed by repeated distillation over barium oxide. A pyridine boiling constantly at 114.3°/738 mm. was obtained. One % of water lowers the b. p. by 3.5°, and smaller quantities in proportion.

The osmotic cell was an inverted thistle funnel with rubber membrane stretched across. No stirring of the solution was possible, but precautions were taken to exclude moisture, as an experiment usually lasted fifteen days or more. A correction was applied for the solvent which passed in and the solute which passed out through the membrane. The osmotic pressure usually attained a maximum and then dropped again. The maximum in no case attained to 5%, and on the average was only 2.7% of that calculated on the gas laws.

Copper oleate, copper chloride, urethane, carbamide, mercuric chloride, and potassium iodide were found to pass through rubber membranes. R. J. C.

**Osmotic Pressure of Colloids. II. Osmotic Pressure of Solutions of Certain Colouring Matters.** WILHELM BILTZ and ARVED VON VEGESACK [and, in part, HANS STEINER] (*Zeitsch. physikal. Chem.*, 1910, 73, 481—512. Compare this vol., ii, 22).—The osmometer already described has been simplified in some respects, and stirring is now found to be unnecessary. Measurements have been made with

Congo-red, night-blue, and benzopurpurin, and the results differ considerably from those previously obtained (*loc. cit.*).

The Congo-red was carefully freed from salts by prolonged dialysis. The osmotic pressure was first measured against a solution of approximately the same electrical conductivity (obtained by concentration of the solution which had passed through the dialyser). The mean molecular weight calculated from these observations was 2333, about three times the normal value, 696, but when measured against pure water in the outer vessel the mean value is about 602, rather less than the normal value, in full agreement with the results of Bayliss (compare *Abstr.*, 1909, ii, 648) obtained in the same way. In no case is a very small molecular weight obtained, corresponding with the fact that Congo-red is considerably ionised, and it is therefore suggested that when only one of the ions is retained by a membrane, the action is due to that ion alone, and when each molecule gives rise to one non-dialysable ion the effect is the same as that of a solution containing only non-ionised molecules. From a consideration of the equilibrium between the ions of the Congo-red and those of the sodium sulphate in the outside solution, the conclusion is drawn that if the solute is not polymerised, the apparent molecular weight should be three times the normal value (that is, 2088), hence the solute is only slightly polymerised, in the ratio 2333 : 2088.

The molecular weight of night-blue is also apparently three times as great when the osmotic pressure is measured against a salt solution of the same conductivity as when it is measured against pure water, but the results in this case are somewhat complicated by hydrolysis.

The molecular weight of commercial Congo-red, which contains about 26% of salts, chiefly sodium sulphate, is about 380, so that the association factor is  $7380/2088 = 3.5$ , and commercial benzopurpurin is still more highly associated. The conclusion that these dyes are more highly associated in the presence of salts is fully confirmed by ultramicroscopic observations.

It is shown by osmotic pressure, ultramicroscopic and viscosity measurements that the degree of polymerisation of night-blue and of benzopurpurin in the presence of electrolytes increases considerably on keeping. Moreover, polymerisation is considerably greater in concentrated than in dilute solutions.

The association factors of night-blue solutions have been determined by osmotic pressure measurements at different temperatures with the following results: 6.7 at 0°, 3.05 at 25°, 2.1 at 50°, and 1.9 at 70°.

G. S.

**Relative Velocities of Diffusion in Aqueous Solution of Rubidium and Cæsium Chlorides.** G. R. MINES (*Proc. Camb. Phil. Soc.*, 1910, 15, 381—386).—A method of determining the relative rates of diffusion of electrolytes is described, in which an aqueous solution of the electrolyte is placed in contact with a solidified 4% solution of gelatin and the rate of diffusion measured by the electrical conductivity at a fixed distance below the surface of the jelly. For dilute solutions the measured conductivities are very nearly proportional to the concentrations, and when the concentration, determined in this manner, is plotted against the time, curves are

obtained which are convex to the base line at the commencement, and slightly concave towards the end of the experiment. Between these limiting regions the concentration increases at a constant rate, the magnitude of which is regarded as a measure of the velocity of diffusion. For 0.1*N*-solutions of lithium, sodium, potassium, rubidium, and caesium chlorides, the relative rates of diffusion were found to be 0.684, 0.830, 1.000, 1.023, and 1.055. These numbers increase as the atomic weight and the velocity of the cation increases.

H. M. D.

[Relative Velocities of Diffusion.] A. V. HILL (*Proc. Camb. Phil. Soc.*, 1910, 15, 387—389).—A mathematical examination of the experimental method described in the preceding paper. It is shown that directly comparable results can be obtained if the depth of the layer of jelly is the same in different experiments. When this condition is satisfied, the intervals of time required to obtain equimolar concentrations are inversely proportional to the diffusion constants of the electrolytes under investigation.

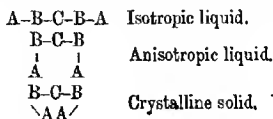
H. M. D.

Molecular Mechanical Theory of Anisotropic Liquids or So-called Liquid Crystals. TH. ROTARSKI (*J. pr. Chem.*, 1910, [ii], 82, 23—37).—After reviewing briefly the characteristic properties of liquid crystals and Quincke and Tammann's theories of their formation, the author develops his own views on the subject. He has already shown (*Abstr.*, 1908, i, 374) that some azoxy-compounds form isotropic, others anisotropic, liquids when fused; the latter resemble nitroso-compounds in several respects, and the author is of opinion that there is a close relation between the formation of liquid crystals and the behaviour of nitroso-compounds during fusion. He explains both by assuming the postulate: the attraction of the constituents of a molecule towards its centre increases with lowering, and decreases with rise, of temperature; thus colourless, crystalline nitrosobenzene and green liquid nitrosobenzene are represented by



and  $\text{—N=O}$  respectively, the group  $\text{—N=O—}$  changing to the chromophore  $\text{—N=O}$ . This explanation is also applicable to the behaviour of *p*-nitrosophenol, aliphatic  $\psi$ -nitroles, and nitrogen peroxide when heated.

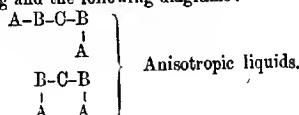
The application of the theory to liquid crystals is as follows. In the solid state the constituents of the molecule are attracted to its centre. When the substance is completely fused to a clear isotropic liquid, the constituents have moved right away from the centre. The intermediate positions, where the constituents have only partly moved from the centre, correspond with the liquid crystalline condition. The three cases may be represented diagrammatically thus:



Substances which form liquid crystals have large molecular weights, and the size of the constituents is favourable to slowness of withdrawal from the centre.

The attraction towards the centre of the molecule, induced by cooling, must depend, not only on the size of the molecule, but also on the magnitude of the attracted groups, because diethylbenzidine forms an anisotropic liquid, whilst dimethylbenzidine is isotropic when fused.

The polymorphism of some anisotropic liquids is sufficiently explained by the preceding and the following diagrams:



C. S.

**Transformation of Amorphous into Crystalline Substances.** CORNELIO DOELTER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 29-34).—In reference to Weimarn's view (Abstr., 1909, ii, 132, 134, 231, 306, and 666) that all solid substances are crystalline and that there is no special amorphous form of matter, the author gives a summary of earlier observations bearing on the subject, and discusses the question from the mineralogical standpoint. Although the evidence appears to be in favour of Weimarn's theory, the author considers that the question of the relationship between the apparently amorphous and the crystalline conditions is not yet settled.

H. M. D.

**Crystalline Solid Solutions as Disperse Systems of Different Degrees of Dispersity.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 35-37).—A quotation from a paper by Frankenheim (*Ann. Physik*, 1860, 111, 1) is given, in which the peculiarities of the structure of mixed crystals are described. From a consideration of these, the author is led to the conclusion that crystalline solid solutions represent disperse systems which can be divided into two groups: (1) disperse systems of lamellar structure; (2) disperse systems of granular structure. The slow rate of diffusion, which characterises the solid state, is favourable to the formation of highly disperse systems.

H. M. D.

**Colloido-chemical Theory of the Constitution of Water.** HEINRICH SCHADE (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 26-29).—On the assumption that water consists partly of polymerised colloidal molecules which undergo dissociation with the formation of simple water-molecules, an attempt is made to explain the abnormal properties of water. Reference is made to the optical properties and the anomalous variation of the density, viscosity, and compressibility with the temperature. With rise of temperature, the colloidal molecules dissociate to a gradually increasing extent. In the colloidal form the water is supposed to have a smaller density and a greater compressibility than water which consists of simple molecules.

H. M. D.

**Colloidal Chemistry of Caoutchouc. II. Theory of Vulcanisation.** WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 45-49).—It is pointed out that the apparently contradictory results obtained in connexion with experiments on the nature of the process of vulcanisation of caoutchouc by Henrichsen and Kindscher (this vol., i, 330) and by Bysow (*Zeitsch. Chem. Ind. Kolloide*, 1910, 6, 281) may be due to the widely different sulphur concentrations which were used in the two series of experiments. Both series of experimental data are consistent with the theory that the sulphur is adsorbed according to an exponential formula.

Reference is also made to Reyckler's experiments on the absorption of sulphur dioxide by caoutchouc (this vol., ii, 272). Although these experiments seem to show that the amount of absorbed sulphur dioxide is proportional to the pressure of the gas, the limits between which the pressure was varied are too narrow to refute the author's supposition that the absorption takes place in accordance with an exponential formula:  $c = K.C^m$ , in which  $m$  is nearly equal to unity.

H. M. D.

**Certain Factors which determine the Constituents of Emulsions of Oil and Water.** T. BRAILSFORD ROBERTSON (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 7-10).—When olive oil and water containing a little alkali hydroxide are thoroughly well shaken, an emulsion is obtained, the nature of which is dependent on the relative proportions of oil and water employed. When the relative quantities of the two substances are changed, the viscous, white emulsion of oil in water is at a particular (critical) point replaced by a much less viscous, yellow emulsion of water in oil. The author has investigated the influence of the concentration of the alkali hydroxide on the critical ratio. The experimental data indicate that above a certain limiting concentration the critical ratio is independent of the concentration of the alkali. The quantity of oil which can be emulsified by a given quantity of water diminishes as the concentration of the alkali hydroxide falls below this upper limiting value until, at a certain lower limiting concentration, the formation of a stable emulsion no longer takes place. The influence of the alkali on the nature of the emulsion formed is supposed to be due to its action on the free acid of the oil. When the amount of alkali in the aqueous layer is more than sufficient to neutralise the free acid, the critical ratio is unaltered. When the quantity of alkali is insufficient to neutralise more than a small proportion of the free acid, a stable emulsion cannot be formed.

H. M. D.

**Appearance of a Maximum and Minimum Pressure with Heterogeneous Equilibria at a Constant Temperature.** F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 31-34).—The author discusses the conditions under which maximum and minimum pressures may occur in the equilibrium between the phases of a binary system at a given temperature.

H. M. D.

**Equilibrium in the System: Sulphuric Acid-Ammonium Sulphate-Water at 30°.** G. C. A. VAN DORP (*Zeitsch. physikal. Chem.*, 1910, 73, 284—288).—The equilibria in the above system have been investigated by solubility measurements, and the results are represented on the usual triangular diagram. The solid substances in equilibrium with the different solutions are:  $(\text{NH}_4)_2\text{SO}_4$ ;  $[(\text{NH}_4)_2\text{SO}_4]_3\text{H}_2\text{SO}_4$ , and  $(\text{NH}_4)\text{HSO}_4$ . G. S.

**Equilibria in the System: Sulphuric Acid-Lithium Sulphate-Water at 30°.** G. C. A. VAN DORP (*Zeitsch. physikal. Chem.*, 1910, 73, 289—290. Compare preceding abstract).—Solubility measurements have shown that the three following compounds,  $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ;  $\text{Li}_2\text{SO}_4$ , and  $\text{LiHSO}_4$ , exist in equilibrium with solutions of the components in different concentrations. G. S.

**Chemical Affinity. The System  $\text{PbCO}_3 + \text{K}_2\text{CrO}_4 = \text{PbCrO}_4 + \text{K}_2\text{CO}_3$ .** H. GOLBLUM and G. STOFFELLA (*J. Chim. phys.*, 1910, 8, 135—188).—The authors have determined the heat developed in the interaction of lead nitrate with potassium chromate in solution to be 10.58 Cal. per equivalent, from which the heat of formation of dissolved lead chromate is 15.23 Cal.

Since the action  $\text{PbCO}_3 + \text{K}_2\text{CrO}_4 \rightarrow \text{PbCrO}_4 + \text{K}_2\text{CO}_3 + 4.98 \text{ Cal.}$  is exothermic, according to Berthelot's view, the mixture  $[\text{PbCrO}_4 + \text{K}_2\text{CO}_3]$  should be the stable one. The product of the ionic solubilities of  $[\text{PbCO}_3 + \text{K}_2\text{CrO}_4]$  is greater than the product of  $[\text{PbCrO}_4 + \text{K}_2\text{CO}_3]$ , hence, according to van't Hoff and Reicher's rule, the latter pair is the more stable.

The four salts cannot exist side by side in presence of their saturated solution, as they would form an invariant system. If the potassium salts are in excess, one of the lead salts, more usually the carbonate, disappears. The equilibrium diagram shows that at one particular concentration of potassium chromate (0.5679% at 25°) the solid residue may contain both lead salts together with potassium carbonate. Both lead salts should exist in contact with solutions in which a certain ratio of carbonate to chromate exists, but which are saturated with neither.

The ratio of dissolved carbonate to chromate in such solutions is the equilibrium constant of Guldberg and Waage. It is, however, not a constant ratio, but decreases with dilution on account of the disturbing effect of ionisation.

No compound or solid solution of potassium chromate and lead chromate is formed, but the solubility of potassium carbonate decreases as the amount of lead carbonate in the solid residue and in solution increases. A double compound of  $\text{K}_2\text{CO}_3 \cdot \text{PbCO}_3$  appears to exist.

On adding lead nitrate solution to a mixed solution of potassium chromate and carbonate, the precipitation of lead chromate or carbonate does not take place in such a way as to produce the pre-determined ratio in the dissolved potassium salts. Whilst the interaction of lead carbonate and potassium chromate proceeds smoothly to an equilibrium, the interaction of lead chromate and potassium carbonate presents

periodic phenomena. The curve representing the amount of potassium chromate formed oscillates with decreasing amplitude until the equilibrium is finally attained. This is attributed by the author to the formation of a basic chromocarbonate of lead. On boiling lead chromate in potassium carbonate solution, an orthorhombic, ruby-red, crystalline solid is obtained with the composition:  $3\text{PbO} \cdot 2\text{CrO}_3 \cdot 2\text{PhCO}_3$ .

R. J. C.

**Ternary Systems with a Ternary Transition Point in the Liquidus-Solidus Diagram.** The System Lead-Cadmium-Mercury. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1910, 73, 328—342. Compare Abstr., 1907, ii, 870).—A general treatment of ternary systems is given, which differs somewhat from that already communicated, inasmuch as it was formerly assumed that more than three kinds of other substances could occur in the system. The statements are illustrated by the system lead-cadmium-mercury; the conclusions and the graphic representations of the equilibria do not differ greatly from those already given. A number of microphotographs illustrating the structure of the different alloys accompany the paper.

G. S.

**Application of Thermal Analysis to Organic Chemistry. I.** PHILIPPE A. GUYE (*J. Chim. phys.*, 1910, 8, 119—130. Compare Scheuer, this vol., ii, 470).—The formation of intermediate additive compounds in organic interactions has not received wider recognition on account of the rarity with which these compounds can be isolated. The author discusses the application of thermal methods, such as the study of the liquidus curve of interacting binary liquid mixtures, to this problem. The method has already been applied by Scheuer to elucidate the allied question of the influence of solvents on rotatory power. It is only applicable when the freezing points of the mixtures are considerably below the temperature at which action sets in, and it is interfered with by the formation of vitreous, amorphous solids. Heating curves and microscopical structure should afford valuable confirmation of the results. The actions hitherto studied have been such as require no catalyst or third substance, as this would necessarily complicate the reasoning.

R. J. C.

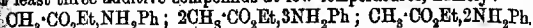
**Molecular Compounds in Binary Organic Systems. A.** WRÓCZYŃSKI and PHILIPPE A. GUYE (*J. Chim. phys.*, 1910, 8, 189—221. Compare Guye, preceding abstract).—Liquidus curves have been determined at temperatures ranging from  $+5^\circ$  to  $-112.5^\circ$ , using a double-walled apparatus like a Beckmann cryoscopic apparatus. The organic mixtures were cooled by placing the double-containing tube in a Dewar vessel containing solid carbon dioxide, ether, or liquid air, according to the case.

Benzyl chloride and anisole, which do not interact, gave perfectly normal liquidus curves. Benzyl chloride and methylaniline, which interact at room temperature, gave a broken f.p. curve showing four compounds and four eutectics in the part studied. The compounds appear to contain benzyl chloride and methylaniline in the molecular ratios 3 : 1, 3 : 2, 2 : 1, 1 : 1.



Ethyl bromide and bromine appear to form an easily dissociated additive compound,  $2\text{EtBr} \cdot \text{Br}_2$ , which is the parent substance of ethylene dibromide.

Ethyl acetate and aniline, which interact to give acetanilide, form at least three additive compounds at low temperatures, namely:



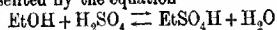
Mixtures containing 20—40% of aniline are extremely viscous, so that perhaps a fourth compound containing 33—40% of acetate is also formed. Viscosity determinations of these mixtures at  $0^\circ$ ,  $-9^\circ$ , and  $-19.5^\circ$  gave unbroken curves, from which no sure conclusion could be drawn. Pyridine and methyl iodide readily combine at room temperature, but there is no evidence of combination when they are brought together at  $-20^\circ$ .

Ethyl ether and ethyl iodide form at a low temperature at least three compounds, presumably of the oxonium type, namely:  $3\text{EtI} \cdot \text{OEt}_2$ ;  $2\text{EtI} \cdot \text{OEt}_2$ ;  $\text{EtI} \cdot \text{OEt}_2$ . The additive products in this case, however, dissociate into their original components, and no double decomposition can be shown to occur.

Chloroform and benzene do not combine, neither do benzene and nicotine. The last is confirmed by the very smooth curve of the rotatory power of nicotine in benzene solution. All the additive compounds observed are more or less dissociated, so that only approximate melting points were obtained for each. Mixtures rich in methyl-aniline or nicotine solidify to a vitreous mass with no true melting point. The same is true for the very viscous solution of 20—40% of aniline in ethyl acetate.

R. J. C.

**Dynamics of the Reaction between Alcohol and Sulphuric Acid.** ROBERT KREMANN (*Monatsh.*, 1910, 31, 245—274).—The equilibrium represented by the equation



has been determined at different temperatures. In the first set of experiments the composition of the equilibrium mixture was determined gravimetrically, the unchanged sulphuric acid being precipitated by means of lead carbonate and the ethyl sulphuric acid determined in the filtrate. In this way it was shown that the reaction is not disturbed by the formation of ether or ethyl sulphate. The mean value of the equilibrium constant,  $K = [\text{acid}][\text{alcohol}]/[\text{ester}][\text{water}]$ , at  $22^\circ$ ,  $55^\circ$ ,  $72^\circ$ , and  $96^\circ$  is 1.74; it is independent of the temperature.

In the second set of experiments the equilibrium composition was determined by direct titration, the mean value being 1.70 at  $40^\circ$  and  $51^\circ$ .

Zaitsechek (Abstr., 1898, ii, 19) in an investigation of the same equilibrium came to the conclusion that a constant could only be obtained on the assumption that the sulphuric acid present existed as the dihydrate. From a consideration of the melting-point curve of the system sulphuric acid-water, the author has calculated the degree of dissociation of sulphuric acid monohydrate, which would be the only one present at the concentrations used, at different temperatures, and finds that the values of  $K$ , calculated on the assumption that this

hydrate is present, are not so good as when hydrate formation is neglected.

The velocity of decomposition of ethyl sulphuric acid in water was measured at 56° and 66°, and found to be approximately proportional to the concentration of the hydrions. The reaction is autocatalytic, but since sulphuric acid is formed as a product of reaction, the concentration of the hydrions remains approximately constant, and the velocity equation simplifies to one of the first order. The constants are satisfactory at the commencement of the reaction, but diminish slightly as the reaction proceeds. The temperature-quotient is abnormally high, namely, 4.5.

The velocity of formation of ethyl sulphuric acid from different mixtures of alcohol and sulphuric acid was measured at 40° and 51°. From the results the velocities of the direct and inverse reactions could be calculated in the usual manner. With increasing concentration of sulphuric acid these velocities go through a weakly-defined minimum, after which they rapidly increase. The latter increase cannot be explained by the increase in the hydrion concentration alone; it must be due to secondary causes, as, for example, hydrate formation, which may have considerable influence kinetically, although it plays no part in the equilibrium.

These two velocities in systems which are initially free from water are about fifty times greater than in aqueous solutions; in 50% alcohol they are slightly greater than in water. In all cases the temperature-quotient is greater than 2. T. S. P.

**Quaternary and Quinternary Systems: The System Alcohol, Ether, Water, Sulphuric Acid, and Ethyl Sulphuric Acid at 0°.** ROBERT KREMANN (*Monatsh.*, 1910, 31, 275—284).—The experimental figures, together with a graphical representation of the same, of the following systems at 0° are given. Ternary: (1) ether-water-alcohol; (2) ether-water-sulphuric acid. Quaternary: (1) ether-water-alcohol-sulphuric acid; (2) ether-water-alcohol-ethyl sulphuric acid. Quinternary: ether-water-alcohol-ethyl sulphuric acid-sulphuric acid. T. S. P.

**Equilibrium between Ammonium Benzoate, Benzamide, and Water.** E. EMMET REID (*Amer. Chem. J.*, 1910, 44, 76—80).—At temperatures between 180° and 220° equilibrium is attained from either side in the reaction represented by the equation  $C_6H_5 \cdot CO_2NH_2 \rightleftharpoons C_6H_5 \cdot CO \cdot NH_2 + H_2O$  when the system contains about 25% of ammonium benzoate. C. S.

**Phase Rule.** R. BOULOUCH (*J. Chim. phys.*, 1910, 8, 113—118).—The phase rule can be deduced from the postulate that equilibrium is independent of the masses of the phases.

The independent components  $c$  in a system, distributed amongst  $\phi$  phases of masses  $\mu_1, \mu_2, \mu_3, \dots$ , have masses  $A, B, C, \dots$ , which obey  $c$  distribution equations of the form  $A = \mu_1 a_1 + \mu_2 a_2 + \mu_3 a_3 + \dots$

The total volume of the system is  $V = \mu_1 v_1 + \mu_2 v_2 + \mu_3 v_3 + \dots$ , where  $v_1, v_2, v_3, \dots$  are the specific volumes of the phases.

... about  $\phi$  equations give ... modified ... therefore ... that is, the system is univariant ...  $\phi$ , the variance  $(c - \phi + 2) = 1$ , that is, ... bivalent, ... temperature and pressure alone are variables, since the volume is completely defined by the values given to  $\mu_1, \mu_2, \mu_3, \dots$ .

If  $c = (\phi - 1)$ , the  $\phi$  masses  $\mu_1, \mu_2, \mu_3, \dots$  can be determined by the  $(\phi - 1)$  distribution equations in conjunction with the volume equation, arbitrarily fixing a value for  $V$ . Pressure will be a function of temperature in this case, so that the system is univariant.

If  $c = (\phi - 2)$ , a solution is only obtainable by reducing the number of unknowns by arbitrarily fixing one of them,  $\mu_x$ . The system is consequently invariant.

When the  $c$  equations are such that complete solution of  $\mu_1, \mu_2, \mu_3, \dots$  cannot be obtained from any set of  $\phi$  of them, one of the quantities,  $\mu_x$ , may be arbitrarily fixed when the remaining  $(\phi - 1)$  follow as functions of it.  $(c - \phi + 1)$  sets of solutions are thus obtainable.

The volume in each case becomes a function of the arbitrarily fixed  $\mu_x$ , so that  $p = f(t)$ , and the condition is that of an indifferent point.

R. J. C.

**Is the Hydrolysis of Cane Sugar by Acids a Unimolecular Reaction when Observed with a Polariscope?** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1910, 32, 885-889).—Polemical. A reply to Julius Meyer (Abstr., 1908, ii, 265; 1910, ii, 403). T. S. P.

**Hydrolysis of Esters of Halogen-substituted Acids.** W. A. DRAUSHEL and J. W. HILL (*Amer. J. Sci.*, 1910, [iv], 30, 72-78).—The esters of chloro- and bromo-acetic acids show no tendency to decompose with liberation of halogen in aqueous solutions of hydrochloric and hydrobromic acid, but from the corresponding iodo-esters in hydroiodic acid solution iodine is set free.

The rate of hydrolysis of a number of alkyl chloro- and bromo-acetates (in  $N/20$ -solution when sufficiently soluble) in the presence of hydrochloric and hydrobromic acids respectively have been measured at 25° and 35°. The rate of hydrolysis is lowered by the introduction of halogen; the relative velocities for acetic, chloroacetic, and bromoacetic esters is 33:21:25. The rates of hydrolysis of different esters of the same acid are in very close agreement.

The temperature-coefficient of the catalytic activity of  $N/20$ -hydrochloric acid is 2.0 between 25° and 35°, and 3.0 between 25° and 40°; the corresponding value for  $N/20$ -hydrobromic acid is 1.7 between 25° and 35°. G. S.

**Simultaneous Reactions in the Decomposition of Ethyl Diazoacetate.** HILARY LACHS (*Zeitsch. physikal. Chem.*, 1910, 73, 291-327. Compare Fraenkel, Abstr., 1907, ii, 746).—It was observed by Fraenkel (*loc. cit.*) that when ethyl diazoacetate undergoes catalytic decomposition to ethyl glycolate in the presence of an acid, such as hydrochloric or nitric acid, the acid is used up in a simultaneous

reaction, resulting in the formation of ethyl chloroacetate or nitroacetate. This point has now been further investigated.

The rates of the two simultaneous reactions have been measured at 15° in 50% alcohol by determining the change of conductivity and the rate of liberation of nitrogen. As catalysts, hydrochloric and nitric acids, in the presence of varying concentrations of the corresponding alkali salts, were used. The acids disappear the more rapidly and the nitrogen liberated is the less in amount, the greater the concentration of the  $\text{Cl}'$  and  $\text{NO}_3'$  ions. With constant hydrogen ion concentration and varying  $\text{Cl}'$  or  $\text{NO}_3'$  ion concentration respectively, the amount of nitrogen liberated is independent of the ester concentration, and depends only on that of the anions. When the liberation of nitrogen has ceased, the double esters (ethyl nitroacetate or ethyl chloroacetate) are only stable in such solutions as contain free  $\text{NO}_3'$  or  $\text{Cl}'$  ions.

An equation containing the ratio of the velocity-coefficient of the decomposition of ethyl diazoacetate,  $k_d$ , to that of the formation of the double ester,  $k_a$ , is deduced, and is shown to represent the experimental results satisfactorily. From this ratio and the known value of  $k_d$ , the rates of formation of the double esters are obtained. The rate of formation of ethyl nitroacetate is proportional to the  $2/3$  power of the  $\text{NO}_3'$  concentration, that of ethyl chloroacetate to the  $4/5$  power of the  $\text{Cl}'$  ion concentration. Under corresponding conditions, the rate of formation of ethyl chloroacetate is about ten times that of the corresponding nitro-ester.

G. S.

**Nature of Neutral Salt Action.** BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1910, 73, 269—283).—In a previous paper (Abstr., 1907, ii, 238) the author has shown that whilst carbon dioxide has very little effect on methyl-orange in water alone, it changes the colour of the indicator to red in the presence of a neutral salt, such as sodium chloride. Veley (*Zeitsch. physikal. Chem.*, 1908, 61, 464) has suggested that this is due to hydrogen ions liberated from the salt by the action of carbonic acid, but this is now shown to be untenable; the total hydrogen ion concentration is greater in a solution of carbon dioxide in water alone than when sodium chloride is present. The sensitiveness of methyl-orange to hydrochloric acid is not affected by potassium chloride in normal solution, but still greater concentrations exert some action.

In order to produce the same tint in corresponding solutions of potassium sulphate and of potassium chloride containing methyl-orange, over six times as much hydrochloric acid must be added to the former solution as to the latter: a result ascribed to some interaction between methyl-orange and  $\text{SO}_4$  ions.

This bearing of neutral salt action on the deviations from Ostwald's dilution law is discussed.

G. S.

**Apparent Chemical Attractions.** RAPHAEL E. LIESEGANG (*Ann. Physik*, 1910, [iv], 32, 1095—1101. Compare Abstr., 1906, ii, 218).—Further observations are described relating to what appears to be chemical action at a distance. If two drops of a sodium hydroxide

solutions are placed at a short distance from one another on a gelatin film containing citric acid and coloured red by the addition of litmus, it is found that the rate of movement of the line of separation of the red and blue regions is considerably greater on the sides of the drops which face each other than on the opposite sides. The fact that this behaviour is the same as that previously observed when drops of silver nitrate were placed on a gelatin film containing sodium chloride indicates that the phenomenon is not connected in any way with the formation of precipitation membranes. The effect is supposed to be due to the more rapid removal of the acid from the region between the drops of the alkali solution.

H. M. D.

**The Shape of the Atom.** R. D. KLEEMAN (*Phil. Mag.*, 1910, [vi], 20, 229—238).—Various consequences are discussed in which the shape of the atom is assumed to be spherical. The sum of the cross-sectional areas of molecules as calculated from this assumption is compared with that found from the kinetic theory for gases at 0°. The gases examined fall into three groups, for each of which an approximately constant ratio between the theoretical and experimental quantities holds. The differences for different groups are ascribed to differences in the arrangements of the atoms and in the amount of external space included in the molecules. Further deductions are made of the coefficients of diffusion of one gas into another, but only a rough approximation between the calculated and experimental values is obtained. It is further pointed out that the mean angle of distribution of secondary  $\beta$ -rays from the direction of the primary  $\beta$ -rays producing them will depend less on the nature of the atom the greater its atomic weight. The results of Bragg and Madsen (*Abstr.*, 1909, ii, 112) on the ratio of the amounts of secondary  $\beta$ -radiation from the two sides of a thick plate penetrated normally by  $\gamma$ -rays are cited as being in agreement with this deduction.

F. S.

**Continuous Absorbing Column.** MAURICE BILLY (*Bull. Soc. chim.*, 1910, [iv], 7, 579—583).—An apparatus is described for the purification, desiccation, or quantitative absorption of gases. In principle it depends on the washing of the gas by a suitable liquid descending over glass balls, contained in a glass tube through which the gas ascends. A reservoir of special form is described, which gives a continuous and regulated flow of the washing liquid, and the removal of the latter after use is provided for by a safety tube of special form. The apparatus is automatic in use, and can be evacuated or cleaned without being dismantled.

T. A. H.

**Separating Apparatus.** C. A. JACOBSON and S. C. DINSMORE (*Am. Chem. J.*, 1910, 44, 84—85).—The apparatus consists of a double-bulbed separating funnel attached by means of a cork in the neck to a pipette siphon. Its advantages are: (i) better and more rapid extraction; (ii) emulsions are not formed so readily; (iii) the upper of two liquids can be siphoned off almost completely when the surface of separation of the two liquids is situated at the constriction

between the two bulbs; (iv) the middle layer of three liquids can be siphoned off without disturbing the other two. C. S.

**The Acetylene Lamp.** [Lecture Experiment.] NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], 82, 183—185).—A description of an acetylene lamp made entirely of glass, so that the working parts can be seen. T. S. P.

**Cooling of Flames.** [Lecture Experiments.] NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], 82, 185—188).—A description of slight modifications of the ordinary experiments showing the action of wire gauze on flames. T. S. P.

**The Striking-Back of the Bunsen Flame.** [Lecture Experiment.] NICOLAE TECLU (*J. pr. Chem.*, 1910, [ii], 82, 189—192).—A description of some experiments to illustrate the striking-back of the Bunsen flame. T. S. P.

## Inorganic Chemistry.

**Presence of Metals and Metalloids in Drinking Waters. Practical Consequences.** FELIX GARRIGOU (*Compt. rend.*, 1910, 150, 1374—1375. Compare this vol., ii, 549).—Most drinking waters contain traces of metals. The author's method of detecting metals of groups III, IV, V, and VI has been applied to more than 3,000 samples, particularly from the Pyrenean basin. A survey of the results shows that the analysis of mineral waters or even drinking waters will often simplify the mineralogical study of a district. The method is particularly useful in revealing metallic lodes. R. J. C.

**Oxygenated Compounds of Fluorine.** GINO GALLO (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 753—755. Compare this vol., ii, 405).—The author has repeated his former experiments, taking additional precautions to exclude the possibility of the presence of hydrogen in the fluorine used, but in this case also a violent explosion occurred four or five minutes after the commencement. Some solid potassium hydroxide which had been introduced into the apparatus did not give any indication of the presence of oxygenated fluorine compounds when examined after the explosion. R. V. S.

**Action of Hydrogen on Sulphur Monochloride and Thionyl Chloride under the Influence of the Silent Electric Discharge.** ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1910, 150, 1752—1754).—On submitting sulphur monochloride to fractionation under atmospheric pressure, partial decomposition occurred with production of sulphur dichloride and sulphur. The monochloride is completely reduced by hydrogen under the influence of the silent electric

hydrogen chloride in the same conditions. On heating, it undergoes a reaction, according to the reaction:  $2\text{S}_2\text{Cl}_2 + 3\text{H}_2\text{O} = 2\text{S}_2\text{O}_3 + 4\text{HCl}$ ; sulphur is also formed through the action of hydrogen sulphide on the monochloride, whilst sulphuryl chloride is also formed, according to the reaction:  $2\text{SO}_2 + 3\text{S}_2\text{Cl}_2 = \text{SO}_2\text{Cl}_2 + 2\text{SOCl}_2 + 5\text{S}$ . In the absence of the discharge, sulphur dioxide slowly reacts with sulphur monochloride at  $160-170^\circ$ , giving sulphuryl chloride and sulphur.

W. O. W.

**Synthesis of Caro's Acid and of Persulphuric Acid.** JOH. D'ARX, and W. FRIEDERICH (*Ber.*, 1910, 43, 1880—1882).—In order to prepare Caro's acid, chlorosulphonic acid is well cooled and the calculated quantity of 100% hydrogen peroxide (compare Abrie, *Abstr.*, 1909, ii, 395) slowly added. When the evolution of hydrogen chloride has ceased, the reaction mass is slowly allowed to become warm, and the dissolved hydrogen chloride sucked off at the pump. The residue then solidifies to a crystalline mass, m. p. about  $45^\circ$ , which can be kept for some days. It consists of Caro's acid, and the synthesis confirms the formula  $\text{HO}\cdot\text{SO}_3\cdot\text{O}\cdot\text{OH}$ .

When treated with another molecule of chlorosulphonic acid, Caro's acid is transformed into persulphuric acid,  $\text{H}_2\text{S}_2\text{O}_8$ . The reaction is best carried out by mixing the calculated quantities of hydrogen peroxide and chlorosulphonic acid, and proceeding as in the preparation of Caro's acid. Crystals of persulphuric acid are obtained, m. p. a little above  $60^\circ$  (decomp.), which can be kept for months. When dissolved in water, it is hydrolysed to a considerable extent into Caro's acid and sulphuric acid.

The authors confirm the formation of perphosphoric acids from hydrogen peroxide (100%) and phosphoric oxide or metaphosphoric acid (compare this vol., ii, 498).

Acetyl chloride gives acetyl peroxide when treated with 100% hydrogen peroxide.

T. S. P.

**Equations and Tables for Saturated and Superheated Nitrogen Vapour.** RUDOLPH PLANK (*Physikal. Zeitsch.*, 1910, 11, 633—643).—The available pressure, volume, and thermal data for nitrogen at low temperatures have been collected and analysed. Tables are given in which the values of various factors are recorded for each  $1^\circ$  between  $-210^\circ$  and  $-182^\circ$ . These factors include the vapour pressure of the liquid, the specific volume of the liquid and of the saturated vapour, the heat content and the entropy of liquid and vapour, the latent heat of vaporisation, and the specific heat of the vapour. The pressure, volume, and temperature data for the unsaturated vapour can be represented by  $v = 30.2T/p - 64.4/T^2$ ; the specific heat by  $C_p = 0.2246 + 0.00038T + 0.005P/T^3$ . The pressure of the saturated vapour corresponds with the equation  $\log p = 3.0 + 0.4 \log T - 289.6/T$ , and the latent heat of vaporisation varies with the temperature according to  $r = 63.85 - 0.2736T$ .

H. M. D.

**Preparation of Anhydrous Hydrazine.** F. RASCHIG (*Ber.*, 1910, 43, 1927).—Contrary to the usual statements in the literature anhydrous hydrazine may be obtained from hydrazine hydrate by

treatment. The mixture is poured into a distilling flask with long side-tube. The flask is heated in an oil-bath in such a way that the temperature takes two hours to rise to  $113^{\circ}$ , the boiling point of hydrazine. By this time all the sodium hydroxide will have dissolved, and the temperature of the bath can be further raised to  $150^{\circ}$ . Anhydrous hydrazine distils over, in almost theoretical quantity, as a strongly fuming liquid, and can be collected in a dry stoppered bottle. It keeps quite well in the bottle, and the stopper does not stick, even on keeping for a long time.

During the distillation, the vapours must not come into contact with cork or rubber, and care must be taken not to inhale them. T. S. P.

**Chemical Action of High Pressure.** Compression of Nitrous Oxide and a Mixture of Nitrogen and Hydrogen; Decomposition of Carbon Monoxide by Pressure. E. BAINEE and A. WRÓCZYŃSKI (*Compt. rend.*, 1910, 150, 1324—1327. Compare this vol., ii, 557).—Nitrous oxide is more stable than nitric oxide, and appears to require a higher temperature to cause any appreciable decomposition. When submitted to a pressure of 600 atmospheres at  $420^{\circ}$ , it suffers a slight decomposition with increase in volume.

Nitrogen and hydrogen do not combine when subjected to 900 atmospheres at the ordinary temperature, although Haber has recently obtained ammonia by the combined action of temperature, pressure, and a catalyst.

Carbon monoxide when compressed under 800 atmospheres at the ordinary temperature does not change, but when compressed under 600 atmospheres at  $320^{\circ}$  undergoes a decomposition with diminution in volume, amounting to 10% in twenty hours. The author points out that the equation  $2\text{CO} \rightarrow \text{CO}_2 + \text{C} + 38.7 \text{ Cal.}$  is exothermic, so that decomposition might be expected. Carbon dioxide was found to be present (5.5% in one case), and a slight greyish-black deposit, perhaps carbon, was noticed. It is suggested that a lower oxide of carbon may have been formed, as Berthelot supposed (compare, however, Gantier, this vol., ii, 605).

The chemical action of high pressures is in favour of the view that catalysis in gases results from the condensing action of the catalytic surface. R. J. O.

**Nature of the Product Described as Black Phosphorus.** DESIRÉ GERNEZ (*Compt. rend.*, 1910, 151, 12—16).—The conversion of phosphorus into a black substance by contact with mercury (Thénard, 1812) was supposed by Blondlot (*Compt. rend.*, 1865, 60, 830; 1870, 70, 836) to be due to the formation of an allotropic modification of phosphorus. The present author describes experiments which appear to show that molten phosphorus is capable of dissolving small quantities of mercury, forming a colourless solution. Such a solution remains colourless when in a state of superfusion, but becomes black, through precipitation of mercury, if caused to solidify. Salts of mercury bring about the same phenomenon, through reduction to the metallic state. W. O. W.



**Preparation and Molecular Weight of Hypophosphoric Acid.** ARTHUR ROSENHEIM and JACOB PROSKER, *Ber.* 1910, 43, 203—204. —Hypophosphoric acid is best prepared by a modification of Corné's method, (Abstr., 1882, 1264) as follows: To 100 grams of copper turnings, contained in a 3-litre flask, are added 100 c.c. of water and 200 c.c. of nitric acid ( $D=1.4$ ). When the reaction is moderated somewhat, stick phosphorus is gradually added until all the copper has been precipitated as a mixture of copper phosphide and spongy copper, the temperature being maintained between  $50^{\circ}$  and  $70^{\circ}$ . The clear, colourless liquid is then decanted off, and half of it neutralised with sodium carbonate; after the addition of the remaining half, sodium hypophosphate,  $\text{NaHPO}_3 + 2\text{H}_2\text{O}$ , separates after a time, the yield being about 10% of the theoretical.

Silver nitrate (compare Abstr., 1883, 1052) does not give such good results as copper nitrate. Zinc, manganese, nickel, cobalt, mercuric and ferric nitrates do not give rise to the formation of hypophosphoric acid, neither do the oxides of nitrogen. When, however, the phosphides of copper, nickel, or silver are used as anodes in 1—2% sulphuric acid, the voltage being 3—10, hypophosphoric acid is produced, in some cases yields as high as 60% being obtained. Iron phosphide produces phosphoric acid only.

Hypophosphoric acid gives a characteristic *guanidine* salt,  
 $(\text{CH}_2\text{N}_3)_4\text{H}_2\text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ ;

white, shining needles, which are soluble in water to the extent of 1.038 grams in 100 c.c. of solution at  $28.5^{\circ}$ . The solution is strongly alkaline. The other acids of phosphorus do not form similar salts.

*Benzyl hypophosphate*,  $(\text{C}_6\text{H}_5)_2\text{PO}_3$ , was obtained as a yellow oil, which could not be distilled, by the interaction of benzyl iodide and silver hypophosphate. The molecular weight in ether was 239—245.

Cryoscopic determinations of the molecular weight of hypophosphoric acid in aqueous solution (compare this vol., ii, 121) point to the formula  $\text{H}_4\text{P}_2\text{O}_6$ , but the authors believe that this is due to association of the simpler molecules  $\text{H}_2\text{PO}_3$ , for the following reasons: the molecular conductivity of aqueous solutions is abnormally high if the formula is taken as  $\text{H}_4\text{P}_2\text{O}_6$ , and the figures so obtained ( $\mu=367.4$  for  $v=31.6$ ;  $\mu=608.8$  for  $v=1111.2$ ) are not in accordance with the properties of hypophosphoric acid. Moreover, the molecular conductivity can only be brought into line with the molecular conductivities of the other acids of phosphorus when the formula is taken as  $\text{H}_2\text{PO}_3$ .

Hypophosphoric acid reacts as a monobasic acid when methyl-orange is used as indicator; with phenolphthalein as indicator, 2 mols. of  $\text{H}_2\text{PO}_3$  are neutralised by 3 mols. of sodium hydroxide.

Hypophosphoric acid monohydrate,  $\text{H}_2\text{PO}_3 \cdot \text{H}_2\text{O}$ , forms rhombic crystals;  $d: c = 0.5635: 1$ ; ca.  $1.7$ . T. S. P.

**Action of Hydrogen on Carbon Monoxide; Formation of Water and Methane. Action of Water at a Red Heat on Carbon Monoxide. Applications to Volcanic Phenomena.** ARMAND GAUTIER (*Compt. rend.*, 1910, 150, 1564—1569. Compare Abstr., 1906, ii, 538). —Hydrogen begins to exert a reducing action on carbon monoxide at  $400^{\circ}$ , water, carbon dioxide, and a little methane

being formed. The reaction is a balanced one, the production of water reaching a maximum at about  $1200^{\circ}$ . At  $900-1000^{\circ}$  the amounts of water vapour and carbon dioxide formed are in agreement with the equation  $4CO + 2H_2 = 2H_2O + CO_2 + 3C$ ; the formation of carbon, however, is not usually observed unless an excess of hydrogen is employed. When a mixture in the proportions  $CO + 3H_2$  was passed through a porcelain tube at  $900^{\circ}$ , the reaction appeared to be represented as  $3CO + H_2 = H_2O + CO_2 + C$ ; but in a second experiment, under apparently identical conditions, no carbon was deposited, the volumes of gaseous products agreeing with the equation  $4CO + 8H_2 = 2H_2O + CO_2 + 3CH_4$ .

The amount of methane formed increases with the proportion of hydrogen, and depends on the rapidity with which it is removed from the sphere of action. Traces of formaldehyde were detected at  $450-650^{\circ}$ , but not above  $950^{\circ}$ .

The author's earlier experiments on the action of carbon monoxide on water vapour at a red heat, have been repeated, and traces of formaldehyde detected amongst the products at  $550^{\circ}$  and  $800^{\circ}$ .

The foregoing reactions are considered to throw light on the occurrence of water, oxides of carbon, methane, and hydrogen in volcanic gases.

W. O. W.

**Action of Iron and Its Oxides on Carbon Monoxide at a Red Heat; Application to Geological Data.** AÉMAND GAUTIER and CLAUDSMANN (*Compt. rend.*, 1910, 151, 16-22. Compare this vol., ii, 607).—The authors have repeated and extended the work of earlier observers on the reduction of carbon monoxide by iron at a red heat.

The production of carbon appears to take place in accordance with the equation:  $3Fe + 28CO = Fe_3O_4 + 16C + 12CO_2$ . The black solid resulting from prolonged action of the gas can be separated by a magnet into two parts, the more magnetic consisting of a mixture of carbides of iron, whilst the residue is carbon with traces of iron. Two carbides approximating in composition to  $Fe_{13}C$  and  $Fe_5C$  have been separated by taking advantage of the greater readiness with which the former dissolves in sulphuric acid. The reaction is represented as  $Fe_3O_4 + 12H_2SO_4 = 12FeSO_4 + CH_4 + 10H_2$ . The carbide  $Fe_5C$  also yields methane, hydrogen, and probably small quantities of cyclic hydrocarbons when treated with sulphuric acid.

The product of the action of carbon monoxide on iron is attacked by steam at a red heat with production of hydrogen, methane, carbon dioxide, and traces of formaldehyde.

W. O. W.

**Isotherms of Monatomic Gases and of their Binary Mixtures. IV. Preparation of Argon. V. Vapour Pressures above  $-140^{\circ}$ , Critical Temperature, and Critical Pressure of Argon.** C. A. CRONNELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, 13, 54-65).—The methods employed for the separation and purification of argon have been examined.

Metallic calcium combines with nitrogen at a low red heat, but the reaction takes place too slowly for use on a large scale. Much better

Argon was obtained with a mixture of calcium, magnesium, and sodium. The mixture of large quantities of oxide argon. For the purification of the mixture of twenty parts by weight of calcium oxide, four parts of magnesium, and one of sodium was found to give good results. The removal of the last traces of nitrogen by combining it with oxygen under the influence of an electric discharge is more conveniently effected by means of an arc between platinum electrodes than by the use of a spark discharge.

Argon can be separated from the small quantities of neon which it contains by fractional distillation at the temperature of liquid oxygen.

Measurements of the vapour pressure and critical data of argon gave the following results, after correction for the small quantities of impurities which the examined gas contained :

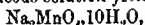
Temperature .....	-140.8°	-134.72°	-129.83°	-125.49°	-122.70°	-122.46°
Pressure in atmos. ...	22.185	29.264	35.846	42.457	47.503	47.890

Critical temperature = -122.44°; critical pressure = 47.996 atmospheres.

H. M. D.

**Sodium Manganate and its Hydrates.** VICTOR AUGER (*Compt. rend.*, 1910, 151, 69—70).—Sodium manganate,  $\text{Na}_2\text{MnO}_4$ , is easily prepared as follows: Sodium permanganate is heated in a silver or platinum dish with twice the calculated quantity of sodium hydroxide. Oxygen begins to be evolved at 115°, and the reaction is complete at 125°. On cooling, the anhydrous manganate separates in black crystals showing a violet reflex. The substance is stable below 170°, but at this temperature loses oxygen, forming a manganomanganate. A solution containing excess of sodium hydroxide deposits large, black prisms of the hydrate,  $\text{Na}_2\text{MnO}_4 \cdot 6\text{H}_2\text{O}$ .

The hydrate,  $\text{Na}_2\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ , resembles the foregoing, and separates from solutions containing 5% of sodium hydroxide. When cooled in a freezing mixture the aqueous solution yields the salt,



as black needles, m. p. 17°; these appear to be isomorphous with sodium chromate.

W. O. W.

**Solubility of Silver Sulphate in Alkali Sulphates.** BARRE (*Compt. rend.*, 1910, 150, 1321—1324).—The solubility of silver sulphate in presence of potassium sulphate and ammonium sulphate increases as the amount of alkali sulphate increases. The same is true of sodium sulphate, below its transition point (33°). Above 33° the solubility of silver sulphate rises to a maximum at a certain concentration of sodium sulphate dependent on the temperature. The solid residue contains not only silver sulphate, but sodium sulphate, the percentage of which increases with its concentration in the liquid phase. Mixed crystals are therefore produced.

The solubility curves for various temperatures all end at a concentration, 40% sodium sulphate, that is, the mixed crystals formed

at this concentration are equally soluble at all temperatures, and have therefore no heat of dissolution. Mixed crystals with more silver salt dissolve exothermally, and increase in solubility with temperature, like pure silver sulphate; mixed crystals with more sodium sulphate dissolve endothermally, and decrease in solubility with temperature like sodium sulphate.

R. J. C.

**The Solubility Influence of Electrolytes.** WALTER HERZ (*Zeitsch. anorg. Chem.*, 1910, 67, 365—368. Compare this vol. ii, 192, 407).—The solubility of barium hydroxide is increased by the presence of alkali chlorides, the effect being greatest with lithium chloride, and least with rubidium chloride. The solubility of cupric sulphate is increased by the presence of sodium and potassium and rubidium chlorides, but depressed by that of lithium chloride. In both cases the order is that of the electro-affinitiss of the cations. Double salts and complex ions must be formed.

C. H. D.

**The Phosphates of Calcium. IV.** FRANK K. CAMERON and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1910, 32, 869—873).—Owing to the confusion regarding the relative stability of the hydrated and the anhydrous dicalcium phosphate, the equilibria existing in the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ , at  $25^\circ$ , have been further investigated. Solutions of phosphoric acid of varying concentration were prepared, and to each solution weighed quantities of potassium chloride and of tricalcium phosphate in sufficient quantity to give a permanent precipitate were added. After equilibrium had been attained, the composition of the solution and of the solid phase was determined. The potassium chloride was added, so that Bancroft's "tell-tale" method (Abstr., 1905, ii, 685; 1909, ii, 147) for determining the composition of the solid phase could be employed.

The composition of the solid phases was found to be  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , with a region between, which was not explored, where the composition of the solid phase was probably  $\text{CaHPO}_4$ . This result is in accordance with Basset's last determination (Abstr., 1908, ii, 675) of the transition interval of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} = \text{CaHPO}_4 + 2\text{H}_2\text{O}$ , but is not in accord with his direct determination of the composition of the solid phases.

The presence of potassium chloride in solutions containing calcium oxide and phosphoric oxide increases slightly the lime content of solutions in equilibrium with dicalcium phosphate and monocalcium phosphate.

T. S. P.

**Initial Temperatures at which Oxides of Metals Give Up Oxygen to Reducing Gases.** IRVING W. FAY, ALBERT F. SEEKER, FREDERICK H. LANE, and GEORGE E. FERGUSON (*Polytechnic Engineer*, 1910, 10, 72—79).—The authors have submitted a number of metallic oxides to the action of hydrogen, carbon monoxide, ammonia, and methane at various temperatures for a period of six hours, and have ascertained the lowest temperatures at which the oxides begin to lose oxygen. The following results were obtained:

Oxide	CO <sub>2</sub>	H <sub>2</sub>	NH <sub>3</sub>	CH <sub>4</sub>
Al <sub>2</sub> O <sub>3</sub> .....	0°	0°	—	—
Ag <sub>2</sub> O .....	and below	and below	—	—
Hg <sub>2</sub> O .....	0	0	—	—
HgO .....	0	80	67°	220°
HgO (yellow)...	0	50	—	—
	and below			
HgO (red) .....	90	115	157	200—210
Pb <sub>2</sub> O .....	—	—	202	202
PbO <sub>2</sub> .....	110	150	198	45
Pb <sub>3</sub> O <sub>4</sub> .....	150	170	above 300	158
PbO .....	160	190	299	210
CuO .....	75	125	225	280
Cu <sub>2</sub> O .....	—	—	208	230
CdO .....	140	—	—	—
ZnO .....	170	—	233	152—159
As <sub>2</sub> O <sub>3</sub> .....	60	—	—	—

**The Action of Hydrogen Sulphide on White Lead.** JULIUS F. SACHER (*Chem. Zeit.*, 1910, 34, 647—648).—Hydrogen sulphide is practically without action on lead carbonate, and carbon dioxide is not evolved during the blackening of white lead. The amount of sulphur taken up by white lead is always less than that required to convert the whole of the lead hydroxide into sulphide, even when the reaction is made as complete as possible. In order to avoid secondary reactions, the white lead is mixed with alcohol, which is then saturated with hydrogen sulphide and removed by evaporation. The analyses agree well with the formula  $4\text{PbCO}_3 \cdot \text{PbS} \cdot \text{Pb(OH)}_2$ , which may be written:  $\text{S(Pb} \cdot \text{CO}_3 \cdot \text{Pb} \cdot \text{CO}_3 \cdot \text{Pb} \cdot \text{OH)}_2$ .

At 85—90°, in presence of water, the whole of the lead hydroxide is converted into sulphide, a little of the carbonate being also converted, owing to previous hydrolysis. Lead sulphate is only blackened in presence of water, owing to hydrolysis; pure lead sulphate in alcohol is unchanged by hydrogen sulphide.

Blackened white lead is not decolorised by light in the absence of moisture. C. H. D.

**Purification of Mercury.** C. J. MOORE (*Chem. Zeit.*, 1910, 34, 735).—In the Lothar-Meyer apparatus for the purification of mercury by letting it fall in fine drops through dilute nitric acid, the author replaces the funnel drawn out to a fine point by a tube shaped like an inverted thistle funnel. Over the mouth of the funnel is fastened a piece of chamois leather, and the mercury is pressed through this to fall in a fine shower through the nitric acid. The stem of the thistle funnel contains a side-tube connected with the reservoir of mercury by means of rubber tubing and a screw-clip; the end of the stem is also closed by means of rubber tubing and clip. Eight % nitric acid is recommended for use in the apparatus. T. S. P.

**The Action of Ammonia on Mercurous Chloride.** HARIDAS SAHA and KUMUD NATH CHOUDEHURI (*Zeitsch. anorg. Chem.*, 1910, 67, 357—360).—"Black precipitate" consists of a mixture of metallic mercury with infusible white precipitate. The latter substance is soluble in concentrated ammonia, and crystallises when the solution is

allowed to evaporate in a vacuum over sulphuric acid. After drying at  $100^{\circ}$  the crystals have the composition  $\text{NH}_2\text{HgCl}$ . It is impossible to assign a formula to the black precipitate, as a part of the white compound contained in it goes into solution, according to the concentration of the ammoniacal liquid. C. H. D.

**The So-called Euxenite Earths.** OTTO HAUSER and FRITZ WIRTH (*Ber.*, 1910, 43, 1807—1812. Compare this vol., ii, 47).—The authors have investigated a number of zirconium minerals in order to see if the zirconia was accompanied by a strange earth, as has been supposed to be the case by Hofmann and Prandtl (*Abstr.*, 1901, ii, 387).

The minerals investigated were zircon, wöhlerite, uhligite, eudialyte, basalt, elaeolite-syenite, sodalite-syenite, katapleite, mosandrite, and natural zirconia. In each case, zirconium hydroxide was obtained from the mineral in an approximately pure condition by the usual methods. This zirconium hydroxide should contain the strange earth, if present. It was therefore fractionated by transformation into the sulphate and hydrolysis of the aqueous solution by boiling, whereby about half the zirconium is precipitated as the basic sulphate (*Abstr.*, 1907, ii, 626). Each of the fractions was examined spectroscopically, and also the equivalent determined. In no case were indications of the presence of a strange earth obtained. T. S. P.

**Basic Nitrate of Yttrium.** CHARLES JAMES and L. A. PRATT (*J. Amer. Chem. Soc.*, 1910, 32, 873—879).—In order to study the system  $\text{Y}_2\text{O}_3\text{--N}_2\text{O}_5\text{--H}_2\text{O}$ , it was necessary to prepare a large amount of pure yttrium oxide, since yttrium nitrate is extremely soluble. To this end, crude yttria earths were first submitted to a long fractional crystallisation by the bromate method (*Abstr.*, 1908, ii, 190, 498). The middle fractions, containing the yttrium, together with a little erbium and holmium, were then precipitated as the hydroxide, which was further converted into the nitrate. The nitrate was then submitted to fractional decomposition, this being carried out by evaporating the solution and fusing the residue until a portion had decomposed. After forty such operations, an yttrium nitrate was obtained of such purity that a layer 12.5 cm. thick of the saturated solution was perfectly colourless, and showed only very faint bands of erbium and holmium.

The equilibrium relations were studied by shaking up solutions of yttrium nitrate of varying concentrations with excess of yttrium oxide at  $25^{\circ}$ . Equilibrium was attained after four and a-half months, after which time the compositions of the various solid phases and solutions were determined.

The only basic nitrate which exists at  $25^{\circ}$  has the formula  $3\text{Y}_2\text{O}_3 \cdot 4\text{N}_2\text{O}_5 \cdot 20\text{H}_2\text{O}$ . It is stable in air, and can exist in contact with water containing more than 33 grams of yttrium nitrate to 100 grams of water.

At  $25^{\circ}$ , 141.6 grams of yttrium nitrate dissolve in 100 grams of water. T. S. P.

Scandium. II. Scandium. *Ann. Chem. Phys.*, 1910, 210, 4, 695, 1909, ii, 44). The preparation and properties of a further number of scandium salts are described. In the majority of cases the salts were prepared by dissolving scandium hydroxide in the acid, or by double decomposition between scandium nitrate and a salt of the acid.

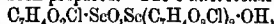
*Scandium iodate*,  $\text{Sc}(\text{IO}_3)_3$ , when washed and dried in the air, is a white, crystalline powder containing  $18\text{H}_2\text{O}$ . Under varying conditions of dehydration, hydrates with 15, 13, and  $10\text{H}_2\text{O}$  have been obtained, and the salt becomes anhydrous on heating at  $250^\circ$ . The *sulphite*,  $\text{Sc}_2(\text{SO}_3)_3$ , is anhydrous, and practically insoluble in cold water; the *borate*,  $\text{ScBO}_3$ , prepared by fusing together scandium oxide and boric acid, is a white powder soluble in dilute acids.

*Scandium aurichloride*,  $3\text{ScCl}_3 \cdot 2\text{AuCl}_3 \cdot 21\text{H}_2\text{O}$ , occurs in yellow, needle-shaped crystals, which are very deliquescent. After prolonged drying in a desiccator over sulphuric acid, an octahydrate is obtained, which changes to the dihydrate on heating for some time at  $100^\circ$ , and to the anhydrous salt on prolonged heating at the same temperature. The *platinocyanide*,  $\text{Sc}_2[\text{Pt}(\text{CN})_4]_3 \cdot 21\text{H}_2\text{O}$ , occurs in monoclinic prisms, crimson by transmitted and green by reflected light; it is soluble in water, forming a colourless solution, and practically insoluble in alcohol. Several lower hydrates appear to exist; the completely dehydrated salt is colourless.

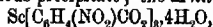
*Scandium chloroacetate*,  $(\text{CH}_3\text{Cl} \cdot \text{CO}_2)_3\text{Sc} \cdot \text{OH} \cdot 2\text{H}_2\text{O}$ , occurs in stellate crystals; the *lactate*,  $\text{Sc}(\text{C}_3\text{H}_5\text{O}_3)_3 \cdot 6\text{H}_2\text{O}$ , in white, feathery crystals, and the *malonate*,  $\text{C}_3\text{H}_2\text{O}_4\text{Sc} \cdot \text{OH}$ , sometimes as a crystalline powder and sometimes amorphous. According to the mode of preparation, the malonate contains 1 or  $2\text{H}_2\text{O}$ . A *basic malonate*,  $\text{C}_3\text{H}_2\text{O}_4[\text{Sc}(\text{OH})_2]_2$ , is obtained when scandium hydroxide is used in large excess. The *malate*,  $\text{C}_4\text{H}_3\text{O}_6\text{Sc} \cdot \text{OH} \cdot \text{H}_2\text{O}$ , occurs in fine granules, which have a mouldy odour; the *fumarate*,  $\text{C}_4\text{H}_2\text{O}_6\text{Sc} \cdot \text{OH} \cdot \frac{1}{2}\text{H}_2\text{O}$ , occurs in microscopic crystals. The *tartrate*,  $\text{C}_4\text{H}_4\text{O}_6\text{Sc} \cdot \text{OH}$ , separates from a boiling solution in colourless crystals; the *racemate*, with  $4\text{H}_2\text{O}$ , comes down less readily on boiling than the tartrate; the *l-tartrate* has been obtained with 1 and  $2\text{H}_2\text{O}$ , and the *meso-tartrate*, with  $1\text{H}_2\text{O}$ , forms a white, granular precipitate.

*Scandium  $\alpha$ -dibromopropionate*,

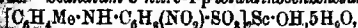
$\text{Sc}(\text{C}_3\text{H}_5\text{O}_2\text{Br})_3 \cdot \text{Sc}(\text{C}_3\text{H}_5\text{O}_2\text{Br})_2 \cdot \text{OH}$ , is a white, amorphous powder. The *citrate*,  $\text{Sc}_2(\text{C}_6\text{H}_7\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ , is much less soluble in hot than in cold water; a dihydrate and tetrahydrate have also been prepared. The *o-chlorobenzoate*,



forms a white, amorphous precipitate; the *m-nitrobenzoate*,



is a white, crystalline powder. The *phthalate*,  $\text{OH} \cdot \text{Sc} \cdot \text{C}_6\text{H}_4\text{O}_2 \cdot \text{H}_2\text{O}$ , is a white, amorphous powder, and loses  $\frac{1}{2}\text{H}_2\text{O}$  on heating at  $110^\circ$  for thirty-six hours. The *tetrachlorophthalate*,  $\text{OH} \cdot \text{Sc} \cdot \text{C}_6\text{Cl}_4\text{O}_2 \cdot 6\text{H}_2\text{O}$ , is also amorphous. *Scandium 3-nitro-4-p-toluidinobenzenesulphonate*,



occurs in feathery, scarlet crystals, which become anhydrous on heating

at 105° the colour being then orange-red. *Scandium octamethyl-tetra-*ortho*-hydroxy-p-dimethylbenzoyl-carboxylate*.



is a red powder.

The scandium used in preparing some of these salts was not spectroscopically pure; the chief object in making the slightly impure specimens being to find out whether a separation of the rare earths had been effected in preparing the salts. G. S.

**Nitrides and Oxides from Aluminium Heated in Air.** EMIL KOHN-ABREST (*Compt. rend.*, 1910, 150, 1757. Compare Abstr., 1905, ii, 637; this vol., ii, 506).—A reply to Serpek (this vol., ii, 615).

W. O. W.

**Metal- and Metallic Oxide-Aluminas and their Use for Catalytic Reactions.** M. KLEINSTÜCK (*Zeitsch. angew. Chem.*, 1910, 23, 1105—1106).—When fibrous alumina (Abstr., 1908, ii, 261) is shaken up with ammoniacal solutions of the chlorides, nitrates, or acetates of various metals, or with colloidal solutions of other metals, adsorption takes place to a considerable extent. If the alumina is then well washed, dried on the water-bath, and finally gently ignited, a mass is left which possesses a characteristic colour depending on the metal used. The colours obtained with copper, iron, manganese, gold, palladium, platinum, chromium, cobalt, nickel, and silver and with various combinations of these are described. Iron- and silver-alumina are both colourless; the former can be used as a delicate test for tannin, and the latter gradually becomes dark violet on exposure to light in the presence of air.

These metal-aluminas may be used for various catalytic purposes; thus copper-alumina oxidises the vapours of methyl-alcohol to formaldehyde, or the hamatoxylin of log-wood extract to hamatein. An aqueous solution of an alkali hydrogen carbonate is reduced by palladium-alumina to formaldehyde and formic acid. Manganese- and platinum-alumina rapidly decompose an aqueous solution of hydrogen peroxide.

T. S. P.

**Electrical Properties of Aluminium Silver Alloys.** WITOLD BRONIEWSKI (*Compt. rend.*, 1910, 150, 1754—1757. Compare Petrenko, Abstr., 1905, ii, 635).—Determinations have been made of the electrical conductivity, temperature-coefficient of resistance between 0° and 100°, thermo-electric power at 0°, variation in thermo-electric power with temperature, and solution potential of a series of aluminium-silver alloys. The results are given in the form of curves, and these are shown to indicate the existence of only two definite compounds,  $\text{Al}_2\text{Ag}_3$  and  $\text{AlAg}_2$ . Petrenko's compound,  $\text{AlAg}_2$ , and Pushin's alloy,  $\text{AlAg}$ , do not appear to be homogeneous substances. W. O. W.

**Oxidation of Aluminium Amalgam.** A. P. ROGER JOURDAIN (*Compt. rend.*, 1910, 150, 1602—1604. Compare this vol., ii, 297).—The following observations appear to point to the existence of a carbonate and peroxide in the substance obtained by exposing aluminium



amalgam in air. On heating one gram of the product in a vacuum, a mixture of carbon dioxide and oxygen were obtained, the amount of the former depending on the proportion of the gas in the atmosphere to which the amalgam had been exposed. No oxidation took place in absence of moisture, but in presence of water vapour, direct absorption of oxygen occurred. The substance dissolved in acids with effervescence, carbon dioxide being liberated and hydrogen peroxide formed. W. O. W.

**Alloys of Cobalt and Silver.** F. DUCELLIEZ (*Bull. Soc. chim.*, 1910, [iv], 7, 506—507).—The alloys were prepared by heating together mixtures of silver and cobalt powders. The properties of the products obtained indicated that they were simple mixtures of the two metals.

The mixtures fused at about the melting point of cobalt, indicating insolubility of silver in cobalt. The silver tended to separate in a pure state; thus a mixture containing 95% of the metal furnished pure silver and an ingot containing 80.77% of this metal. All the alloys were attacked by hydrochloric acid; those rich in cobalt leaving silver powder, those moderately rich in cobalt giving lamellae of silver, whilst those poor in cobalt retained their shape, but became brittle, and after treatment with the acid could be broken up by a hammer. On liquation, at a temperature intermediate between the melting points of the two metals, of an ingot containing 70.25% of silver, a drop of pure silver was obtained, and the lower part of the ingot became richer in silver. All the alloys were magnetic. After treatment with hydrochloric acid the surfaces of the alloys examined under the microscope showed (1) grey zones, often elongated, especially in those rich in cobalt, and (2) brilliant zones corresponding with silver. No eutectic product was observed. In a normal solution of cobalt sulphate the alloys furnished no *E.M.F.* with cobalt poles, but gave a constant *E.M.F.* of 0.535 volt with silver poles. T. A. H.

**Alloys of Nickel and Silver.** ÉMILE VIGOUROUX (*Bull. Soc. chim.*, 1910, [iv], 7, 621—622).—Alloys poor in silver are magnetic, slightly malleable, apparently homogeneous to the naked eye, but spongy and clearly heterogeneous when examined microscopically. When 50% or more silver is present, particles of this metal become visible to the naked eye. An alloy containing 70% of silver on re-melting separates into pure silver and nickel, containing 1.6% of silver. The alloys are attacked by hydrochloric acid, the nickel being dissolved, and silver left as a residue. With nickel poles in a normal solution of silver sulphate an *E.M.F.* varying from -0.0021 to +0.0168 volt is developed, and with silver poles an *E.M.F.* ranging from -0.3962 to -0.4382 volt, under otherwise similar conditions, indicating that the alloys are merely mixtures of the two metals (compare Ducelliez, preceding abstract). There is evidence of the formation of a weak solid solution of silver in nickel. T. A. H.

**Solutions of Blue Molybdenum Oxide.** A. DUMANSKI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 20—21).—When molybdenum trioxide, suspended in water, is heated on the water-bath with a large excess of

powdered metallic molybdenum, a solution of the oxide  $\text{Mo}_2\text{O}_5$  is obtained, which, according to cryoscopic measurements, contains unpolymerised molecules of the oxide. On addition of ammonium chloride, barium chloride, and other salts to this solution, polymerisation takes place, and the oxide passes into the colloidal form.

H. M. D.

**Extraction of Germanium from Blendes.** GEORGES URBAIN, M. BLONDEL, and OBLEDOFF (*Compt. rend.*, 1910, 150, 1758—1760. Compare Abstr., 1909, ii, 1026).—Experimental details are given for extracting germanium from blendes containing traces of this element. After isolating a mixture of the sulphides of arsenic, molybdenum, and germanium, this is dissolved in the minimum amount of ammonia and the solution fractionally precipitated by acid of diminishing concentration. The whole of the arsenic and molybdenum is thus precipitated, leaving germanium in solution. Five grams of pure germanium have been obtained from 550 kilograms of a Mexican blende.

W. O. W.

**Theory of the Preparation of Thorium Salts. I. Purification by means of the Sulphate.** IWAN KOPPEL and H. HOLTkamp (*Zeitsch. anorg. Chem.*, 1910, 67, 266—292).—In the purification of thorium salts, the anhydrous sulphate is dissolved in water, yielding a highly supersaturated solution, from which a hydrate separates spontaneously. It has been shown by Roozboom (Abstr., 1890, 686) that the octa-hydrate is at all temperatures labile with respect to the nona-hydrate, but the two solubility curves are very close to one another, and in practice the octa-hydrate is always obtained. In the technical method, the hydrated sulphate is precipitated by adding sulphuric acid to a concentrated solution of the chloride. The conditions of precipitation have now been investigated.

The formation of the tetra-hydrate must be avoided, on account of its bad filtering qualities, and of its considerable solubility in water at the ordinary temperature.

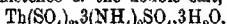
The solubility of thorium sulphate octa-hydrate in dilute sulphuric acid of different concentrations has been studied at 20°, 30°, and the boiling point. In each case the solubility falls with the concentration of the acid until 0.5%  $\text{H}_2\text{SO}_4$  is reached, then rises to a maximum near 4%  $\text{H}_2\text{SO}_4$ , and again falls. When 33%  $\text{H}_2\text{SO}_4$  is reached, the solid phase is converted into the tetra-hydrate at 30°, beyond which concentration the solubility is very small, and acid salts are formed. The solubility of thorium sulphate in nitric and hydrochloric acids at 30° shows maxima at 17%  $\text{HNO}_3$  and 4.5%  $\text{HCl}$  respectively; minima are not observed. The presence of phosphoric acid in a solution in hydrochloric or nitric acid retards the precipitation of the sulphate, and also increases the solubility, so that when the quantity of phosphoric acid reaches 0.73 mol.  $\text{P}_2\text{O}_5$  to 1 mol.  $\text{ThO}_2$ , sulphate is not precipitated. The crystallisation of the sulphate is slow, being incomplete after twenty-five hours. Raoult's law is found to be applicable to the vapour pressures of the hydrates and their solutions.

Hydrochloric acid is to be preferred to nitric acid for dissolving the

thorium sulfate precipitates in the presence of an excess of solvent acid is without influence. The quantity of sulphuric acid should be 0.5% in excess of that theoretically required, and, in order to prevent the formation of the tetra-hydrate, the temperature must be below 42°, and preferably much lower.

The density and refractive index of solutions of pure thorium nitrate have been determined and tabulated. C. H. D.

**Double Sulphates of Thorium.** BARRE (*Compt. rend.*, 1910, 150, 1599—1602).—The solubility curve for thorium sulphate in solutions of potassium sulphate of different concentrations at 16° shows branches corresponding with the following double salts, each of which has been isolated and analysed:  $\text{Th}(\text{SO}_4)_2 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , slender, interlacing needles;  $\text{Th}(\text{SO}_4)_2 \cdot 2\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , triclinic crystals (compare Berzelius, *Ann. Chim. Phys.*, 1830, [ii], 43, 5);  $\text{Th}(\text{SO}_4)_2 \cdot 3.5\text{K}_2\text{SO}_4$ , small, triclinic crystals. The curve for thorium sulphate in solutions of sodium sulphate shows a maximum corresponding with the concentration 2.98% of  $\text{Na}_2\text{SO}_4$ ; the only compound isolated was Cleve's salt;  $\text{Na}_2\text{Th}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . The curve for solutions in ammonium sulphate shows three branches, agreeing with the existence of the double salt,



large, monoclinic prisms, and of the salts,  $(\text{NH}_4)_2\text{Th}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , described by Rosenheim, Samter, and Davidsohn (*Abstr.*, 1903, ii, 601). W. O. W.

**Decomposition of Thorium Sulphate by Water.** BARRE (*Compt. rend.*, 1910, 151, 70—72).—Demarçay (*Abstr.*, 1883, 1053) obtained a basic salt by the action of water on thorium sulphate, to which he attributed the composition  $\text{Th}_4(\text{SO}_4)_3 \cdot 0.8\text{H}_2\text{O}$ . This substance, however, appears to be a mixture of thorium sulphate with a basic salt,  $\text{ThO}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$ . The latter has been obtained crystalline by allowing Demarçay's product to remain in contact with water for a long time; 100 parts of water at 100° dissolve 0.023 part of the salt.

W. O. W.

**The Atomic Weight of Vanadium. II. The Chlorine Content of Vanadium Oxytrichloride and the Ratio  $\text{V}_2\text{O}_5 : \text{V}_2\text{O}_3$ .** WILHELM PRANDTL and BENNO BLEYER (*Zeitsch. anorg. Chem.*, 1910, 67, 257—266. Compare this vol., ii, 134).—A further series of four estimations of chlorine in vanadium oxytrichloride, four others being rejected, gave a mean value of  $61.3348 \pm 0.0087\%$  Cl, or  $51.061 \pm 0.024$  for the atomic weight of vanadium.

Vanadium pentoxide was prepared by distilling vanadium oxytrichloride into pure water, evaporating the solution, and gently heating the moistened residue until free from hydrogen chloride. The residue was then repeatedly moistened with nitric acid and heated to just below the melting point, finally fusing in a platinum boat in a stream of oxygen, yielding very long, glistening, brownish-red crystals, *mp.* 3357.

The reduction by hydrogen took place in a large platinum boat in a glass tube, the temperature being kept low at first and gradually

raised, in order to avoid fusion, yielding a black powder of vanadium trioxide,  $51.870$ . Owing to the very rapid oxidation of the trioxide it was necessary to transfer the boat to a weighing tube in an atmosphere of hydrogen. Even in this way an entirely constant weight could not be attained. As a control, the trioxide was heated in oxygen until constant in weight. The atomic weight thus obtained for vanadium,  $51.374 \pm 0.033$ , may be too high, owing to the presence of a higher oxide than the pentoxide, and is in any case uncertain.

C. H. D.

**Behaviour of Platinum and Nickel Wires to Hydrogen at High Temperatures.** MARCELLO VON PIRANI and ALFRED R. MEYER (*Zeitsch. Elektrochem.*, 1910, 16, 444—447).—The resistance of a nickel wire increases when it is heated to a high temperature in a current of hydrogen; in the case of platinum the melting point is depressed by  $250^\circ$  to  $300^\circ$ , and the metal becomes brittle.

It is shown that the effect is not due to occlusion of hydrogen; it is not due to diffusion of furnace gases through the quartz tube used (if nitrogen is used instead of hydrogen it is not observed), and, further, the changes do not take place in a limited quantity of hydrogen. It is thought that the changes are probably due to the presence in the hydrogen of a small quantity of an impurity containing carbon, from which the metals take up carbon at or near their melting points.

T. E.

## Mineralogical Chemistry.

**Vanadium Deposits in Peru.** D. FOSTER HEWETT (*Trans. Amer. Inst. Mining Engineers*, 1910, 40, (1909), 274—299).—The modes of occurrence and characters of deposits of vanadium ores at two distinct localities in Peru are described. In the Yauli district in province Tarma, a black, lustrous asphaltite occurs as a large, lenticular mass in sedimentary rocks of Mesozoic age. This has been previously described by Torrico y Meca as a vanadiferous coal (Abstr., 1896, ii, 276). As shown by a large series of analyses, the material varies widely in composition: moisture,  $0.08$ — $7.83$ ; volatile matter,  $8.26$ — $49.02$ ; free carbon,  $31.15$ — $90.58$ ; S,  $1.87$ — $44.59$ ; ash,  $0.64$ — $17.80$ ;  $V_2O_5$ , trace— $1.43\%$  ( $V_2O_5$  in ash,  $2.3$ — $64.3\%$ ).

In the Quisque (or Minasragra) district in province Pasco (Abstr., 1907, ii, 788) the vanadiferous minerals form a thick, lenticular vein in red shales of Cretaceous age, and are associated with dykes of igneous rocks. The central portion of the vein is composed of patronite (D  $2.65$ — $2.71$ , H  $2\frac{1}{2}$ ), the outer portions of quisquite (D  $1.75$ , H  $2\frac{1}{2}$ ), while between the two are bands of a coke-like material (D  $2.4$ , H  $4\frac{1}{2}$ ). Analyses of purer patronite than that examined by W. F. Hillebrand gave  $19.3$ — $24.8\%$  vanadium; the formula  $V_8S_8 + nS$  is suggested.

By the oxidation of these ores, several secondary vanadium minerals are formed in abundance, and the mine-waters contain vanadium in solution. Preliminary descriptions, with partial analyses by W. F. Hillebrand, are given of red, brown, and green hydrated vanadium oxides and of a hydrated calcium vanadate. Some of these appear to represent new species (compare Neoadkevitch, Abstr., 1909, ii, 411).

L. J. S.

**Mineralogical Constitution of French Phosphorites.** ALFRED LACROIX (*Compt. rend.*, 1910, 150, 1213—1217).—Carnot has shown that many French phosphorites supposed to be fibrous forms of apatite are deficient or lacking in fluorine. Microscopical examination reveals three types: (1) a holocrystalline variety which is always fibrous; (2) an isotropic variety in thin, colourless or yellow, homogeneous sheets; (3) a mixture of crystalline and isotropic matter.

Analyses of the best samples of (2) and (3) showed that they were very similar, consisting mainly of calcium phosphate and calcium carbonate with a little fluoride. The microscopical and chemical properties agree with the assumption that the mixtures are closely related to dahllite  $[\text{Ca}_3(\text{PO}_4)_2, \text{CaCO}_3, \frac{1}{2}\text{H}_2\text{O}]$ , and francolite  $[\text{Ca}_3(\text{PO}_4)_2(\text{CaF})_2, \text{CaCO}_3, \text{H}_2\text{O}]$ .

It is suggested that Damour's hydroapatite is also a variety of francolite, the carbonic acid having been overlooked by Damour.

Colophanite from the Guano deposits in the Island of Sombbrero is practically identical with the isotropic phosphate in the French deposits.

A new nomenclature is suggested for the phosphorites. Isotropic compounds of phosphate and carbonate are classed as *colophanites*, and mixtures of colophanite with optically negative, crystalline matter of similar composition are termed *quercyites*. A rarer form has been noticed in samples from Sombbrero and Badajos, but seldom in French samples, in which both positively and negatively birefringent crystals are mixed with the colophanite. This is termed *β-quercyite*.

R. J. C.

**[Identity of Pastreite with] Jarosite.** AZÉMA (*Bull. Soc. franç. Min.*, 1910, 33, 130—132).—The following new analyses of pastreite (Norman, 1866) from Saint-Félix-de-Pallières, dep. Gard, shows the presence of alkalis, and proves the identity of the mineral with jarosite  $\text{K}_2\text{O} \cdot 3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{K}_2[\text{Fe}(\text{OH})_2]_2(\text{SO}_4)_4$ . The mineral forms ochre-yellow, compact masses with a conchoidal fracture, and under the microscope it is seen to consist of minute crystals with strong negative birefringence. When heated to redness, it turns brown and gives off sulphur trioxide. It owes its origin to the action of the products of oxidation of iron-pyrites on the gangue:

SO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	H <sub>2</sub> O	Insol.	Total.	Sp. gr.
24.02	48.63	7.75	0.55	10.61	0.29	99.35	3.02

L. J. S.

**Silicate Fusions with Artificial Mixtures.** VERA HAEMMERLE (*Jahrb. Min.*, 1910, *Beil.-Bl.*, 29, 719—738).—In many of the previous experiments made with silicate fusions, the materials employed consisted of natural minerals; these are, however, never quite pure, and any unfused particles may exert an influence on the crystallisation of the mass. In the present experiments, pure chemicals (silica, magnesia, calcium carbonate, sodium carbonate, and aluminium hydroxide) were fused together in the proportions required by olivine, diopside, and labradorite, either alone or in the presence of natural magnetite. Mixtures of these materials corresponding with labradorite (20—80% in different fusions) and diopside (80—20%), together with 10% magnetite, resulted in the formation of the following minerals, which were determined under the microscope in thin sections of the product: diopside, soda-augite, alumina-iron-augite, hedenbergite, labradorite, anorthite, magnetite, spinel, and haematite; and mixtures corresponding to olivine, labradorite, and diopside, in various proportions, gave olivine, diopside, alumina-augite, labradorite, and nepheline. These results, which agree with those obtained when natural minerals supplied the materials fused together, point to various chemical reactions in the dissociated fused solutions.

L. J. S.

**Hornblende and Augite from the Rhön Basalts.** XENIA GALKIN (*Jahrb. Min.*, 1910, *Beil.-Bl.*, 29, 681—718).—The basaltic rock, tufts, and agglomerates of the Rhön Mountains contain large, well-developed crystals of hornblende and augite, which become isolated on the weathering of the rocks. Both minerals often occur together in the same rock. Seven analyses were made of hornblende crystals from different localities; these vary only slightly amongst themselves, and the mean is given under I. Under II is the mean of five analyses of augite from various localities:

	SiO <sub>2</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O	Total
I.	40.65	3.76	0.88	13.87	8.36	4.57	12.34	12.23	2.27	1.74	0.45	100.52
II.	47.56	1.54	0.48	5.28	6.94	3.05	11.76	22.14	1.09	0.38	0.22	100.44

These analyses, together with others, are discussed at length in connexion with the formulæ proposed by Tschermak, Scharizer, Rosenbusch, and Penfield, but no definite conclusions are clearly stated.

L. J. S.

**Anophorite, a New Hornblende from the Katzenbuckel.** WILHELM FREUDENBERG (*Mitt. Badischen Geol. Landesanstalt*, 1908, 6, 15—84).—A detailed description is given of a variety of alkali-hornblende occurring as needles in basic streaks in the shonkinite rock of the Katzenbuckel in Baden. The pleochroism, *c* (deep reddish-brown) > *b* (green to yellowish-green) > *a* (straw-yellow), resembles that of cataphorite, but there are differences in optical orientation; in anophorite the plane of the optic axes is perpendicular to the plane of symmetry, and the angle of extinction, *b*:*c* = 20—28°, is less than in cataphorite. The etched figures are described in detail.

The following analysis, by O. N. Heidenreich, also shows differences

**Chemistry of Submarine Glauconite.** WILLIAM A. CASPARI (*Proc. Roy. Soc. Edin.*, 1910, 30, 364—373).—Glauconitic green sand when digested first with hydrochloric acid and then with sodium hydroxide solution and shaken with boiling water yields a colloidal suspension of disintegrated glauconite; this, on addition of a trace of acid, gives a green, flocculent precipitate. Material containing varying amounts of calcium carbonate (5—33%) and quartz and other mineral grains (3—47%) was so treated, and the separated glauconite analysed, with the following results: (I) of material dredged from the Pacific off Panama at a depth of 556 fathoms, and (II) from the Agulhas Bank at 110 fathoms:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	K <sub>2</sub> O	Loss on ignition	Total
I.	49.12	7.09	25.95	0.89	3.10	7.02	7.12	100.29
II.	51.15	7.61	18.83	2.79	4.54	7.80	7.56	100.27
III.	56.90	—	28.16	4.16	—	7.27	4.19	100.58

Including aluminium with ferric iron, and calcium, magnesium, and ferrous iron with potassium, these analyses agree fairly well with the formula  $\text{KFeSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$  (compare Collet and Lee, *Abstr.*, 1906, ii, 170).

Under the microscope, grains of glauconite show a yellowish-green, birefringent material enclosed in a black, isotropic network of organic matter. The latter, when dissolved out by sodium hydroxide solution, gave C 54.85%, H 5.79%; it resembles humic acid. Glauconite possesses the property of absorbing dyes, as do clays and zeolites; and it also absorbs water from a moist atmosphere, being capable of holding up to 30.35%  $\text{H}_2\text{O}$ . It is therefore suggested that glauconite is a colloidal silicate, the pleochroism and optical birefringence being probably the result of strain set up by the network of organic matter.

An artificial product resembling glauconite was obtained by mixing colloidal solutions of a complex ferric radicle (potassio-ferric tartrate) and potassium silicate; the clear, greenish-blue jelly so formed was heated under pressure at 180° for some hours, when grass-green, flocculent particles separated; this gave analysis III above. The presence of an organic acid (no doubt humic acid in nature) appears to be essential for the formation of glauconite.

L. J. S.

**The Fireclay [and Sideropileite] of Glenboig, Lanarkshire.** JOHN WALTER GREGORY (*Proc. Roy. Soc. Edin.*, 1910, 30, 348—360).

The Glenboig fireclay forms a bed, six feet in thickness, in the shales and sandstones of the millstone-grit series. Unlike the fireclays of the coal-measures, it is not overlain by a bed of coal, neither does it contain any fossil roots of plants. The fine-grained clay-substance forming the bulk of the material is present as minute, rounded granules, about

0.001 mm. diameter; it is amorphous, and not crystalline, and is preferable to halloysite rather than to kaolinite (see following abstract). Embedded in it are abundant grains of quartz, some grains of feldspar, and minute, lenticular, zoned crystals of a rhombohedral carbonate. Analysis, by D. P. McDonald, of the last shows it to be the sideroplastic variety of chalybite, with  $\text{FeCO}_3$ , 88.4,  $\text{MgCO}_3$ , 8.3,  $\text{CaCO}_3$ , 3.3%.

$\text{CO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{FeO}$	$\text{Fe}_2\text{O}_3$	$\text{H}_2\text{O}$	Insol.	Total.	Sp. gr.
33.28	1.56	3.39	46.45	6.49	[0.79]	8.06	100.00	3.63

L. J. S.

Nature of the Clay-substance of Fireclay of Glenboig, Lanarkshire. DAVIN P. McDONALD (*Proc. Roy. Soc. Edin.*, 1910, 30, 374—377. See preceding abstract).—The finest material separated by repeated washing from the fireclay was dried in a steam-oven and analysed with the following results. The dried material had a decided buff colour, and under the microscope some free quartz was detected:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$ (+ $\text{Fe}_2\text{O}_3$ )	$\text{CaO}$	$\text{MgO}$	$\text{H}_2\text{O}$ at 105°	$\text{H}_2\text{O}$ combined.	Total.
46.67	37.65	0.16	n. d.	2.13	12.66	99.27

This analysis points to either kaolinite or halloysite, although the water percentage is slightly higher than that (14.0) required by the kaolinic formula  $2\text{H}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . The facts that the material is amorphous and is decomposed by acid suggest, however, that it is halloysite rather than kaolinite. When the washed clay is boiled with strong hydrochloric acid for two hours, 6.5%  $\text{Al}_2\text{O}_3$  goes into solution, and after thirteen hours 36.6%  $\text{Al}_2\text{O}_3$  is dissolved. Halloysite from Dordogne yielded 2.2%  $\text{Al}_2\text{O}_3$ , and lenzinite from the Eifel 21.97%, after two hours' boiling with hydrochloric acid.

L. J. S.

Study of Laterites. H. ARSANDAUX (*Compt. rend.*, 1910, 150, 1698—1701).—The laterites examined are supposed to be normal muscovites in which water of constitution has progressively replaced the alkalis. Analysis of a series of more or less exposed samples from the same bed confirms this view.

A progressive secondary change gradually replaces the silicates with hydrated oxides of iron and aluminium, the proportion of the latter being greater the nearer the micaceous products are to kaolinite. Part of the hydrated alumina appears to be formed directly from the muscovite, and part passes through the intermediate stage of kaolinite.

R. J. C.

The Amount of Thorium in Sedimentary Rocks. I. Calcareous and Dolomitic Rocks. JOHN JOLY (*Phil. Mag.*, 1910, [vi], 20, 125—128).—Thirty-four rocks, mainly limestone, chalk, dolomite, marble, and oolite, were examined for thorium by methods previously employed, but detectable quantities were found only in six specimens, the maximum quantity being only  $0.22 \times 10^{-6}$  gram of thorium per gram. The amount detectable was from 0.03 to 0.06, according to the quantity of material dealt with. It would appear



from these results that thorium of which  $0.9 \times 10^{-10}$  gram has been found per gram of sea-water from the Indian Ocean, is selectively rejected in the organic processes attending the abstraction of the lime.  
7. S.

## Physiological Chemistry.

**The Fundamental Bodily Needs of the Infant, as Determined by Measurement of the Gaseous Exchange.** ARTHUR SCHLOSEMANN and HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1910, 26, 14-40).—The gaseous exchange in various infants during a period of fasting, and when at complete rest, was determined. Under these conditions it was found that the infant produced, on an average, 12 grams of carbon dioxide per square metre of body surface, and consumed 11 grams of oxygen. The nitrogen excreted was also estimated, and from the numbers obtained, the amount of fat and carbohydrate consumed was estimated. It was found that a child of 4326 grams weight consumed 273 calories in twenty-four hours when kept at a temperature of  $20^{\circ}$ .  
S. B. S.

**Influence of Oxygen Inhalations on Muscular Work.** LEONARD E. HILL and MARTIN FLACK (*J. Physiol.*, 1910, 40, 347-372).—A full account of researches of which several preliminary communications have already been published. They support the authors' contention that inhalation of oxygen is beneficial to athletic work.  
W. D. H.

**Action of Certain Substances on the Respiratory Centre.** ARTHUR S. LOEVENHART and W. E. GROVE (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xvi-xvii).—Sodium iodosobenzoate cannot oxidise phenolphthalein to phenolphthalein, but it can do so in the presence of serum. The oxygen united to the iodine in iodosobenzoic acid is, therefore, capable of physiological utilisation. This is supported by the effects of iodoxybenzoate or iodosohydroxybenzoate when injected intravenously in animals; the respiratory centre is very sensitive to changes in oxidative processes, and it is immediately and markedly depressed. This leads to apnoea, recovery from which is spontaneous. The taste of sodium iodosobenzoate is further indistinguishable from that of hydrogen peroxide, and is probably in both cases due to the action of active oxygen on the end-organs of taste.  
W. D. H.

**The Estimation of the Quantity of Blood by means of the "Critical Method."** EMIL ABDERHALDEN and JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1910, 66, 120-127).—The principle of the method consists in estimating the change in the rotation of the plasma produced

by injecting an optically active substance. Substances suitable for this purpose must have a high rotatory power, be easily soluble in isotonic saline, in which solution they should not cause marked change in the rotatory of the blood, and should be non-toxic. Dextrin fulfils these conditions, and by the method it was calculated that the amount of blood in different dogs varied between 11.3 and 12.4% of the total body-weight. The blood should be withdrawn at as short an interval as possible after the injection of the dextrin. S. B. S.

**The Action of Pure Choline on Blood Pressure.** ERIC ARDERHALDEN and FRANZ MÜLLER (*Med. Klinik.*, 1910, No. 22. Compare this vol., ii, 530).—Further data are given which support the authors' statement that the typical effect choline produces on arterial blood pressure is a lowering. This is partly due to action on the heart, but mainly to dilatation of peripheral vessels. The drug, however, is believed to act on both varieties of vaso-motor nerves, and this not until the vaso-dilators are paralysed by atropine that the effect on the vaso-constrictors is seen. W. D. H.

**Vasotonin, a New Drug which Lowers Blood Pressure.** FRANZ MÜLLER and BRUNO FELLNER (*Therapeut. Monatsheft.*, 1910, 24, Jude).—The name vasotonin is given to a combination of yohimbine and urethane, which produces a fall of blood pressure due to vasodilatation, and appears to have considerable therapeutic value. W. D. H.

**Peritoneal Blood Transfusion.** ARTHUR E. BOYCOTT (*J. Path. Bact.*, 1910, 14, 605—614).—Blood transfused into the peritoneal cavity and subsequently absorbed into the circulation is destroyed more quickly than blood transfused directly into the veins. This may be due to the red cells being rendered relatively more foreign by their passage through an extravascular position. The mechanism of destruction is the same, except that phagocytosis of red cells in the lymph glands and spleen is more prominent. W. D. H.

**Anticoagulants and Frog's Blood.** HAROLD PRINGLE and JOHN LAIT (*Proc. physiol. Soc.*, 1910, xxxv—xxxvi; *J. Physiol.*, 40).—In Amphibia as in Crustacea, blood coagulation consists of two events: the first, connected with the coagulation, caused by thrombocytes or explosive cells, and the second, a general jellying of the plasma. Snake venom, peptone, and novocaine prevent both occurrences. In the case of the two first-named anticoagulants, the amoeboid movements of the leucocytes are marked; with novocaine they are slight or absent. In coagulation *in situ* at a wound in a tadpole's tail, both agglutination of thrombocytes and a localised coagulation may be observed. W. D. H.

**Blood Coagulation in the Amphipod, Gammarus.** JOHN LAIT (*Proc. physiol. Soc.*, 1910, xli; *J. Physiol.*, 40).—The local stoppage of a wound in *Gammarus* is due to cell agglutination, and this is the only visible factor in specimens from the upper tide limit.

...the explosion of the ...  
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D. H.

**The Reaction of Blood to Silver Hydrosol.** GIACCHINO (Zentr. Physiol., 1910, 24, 253-258).—The precipitating substance in the blood is thermostable, and occurs in the red corpuscles; its action varies with the amount of haemoglobin, but the thermostability is against the material being haemoglobin. W. D. H.

**The Composition and Properties of White-Blood Corpuscles.** STEFANO MANGINI (Biochem. Zeitsch., 1910, 23, 140-148).—The leucocytes were obtained by allowing large quantities of oxalated horse blood to remain in tall cylinders, mechanically separating the layer of white corpuscles thus formed, and then washing them repeatedly with physiological saline containing a little toluene and minute quantities of ammonium oxalate, which substance inhibits clotting. From 30 litres of blood, 30 c.c. of moist leucocytes could be obtained, which contained appreciable quantities of calcium oxalate. The leucocytes were, with exception of a small residue, soluble in 0.1% sodium carbonate, from which solution a precipitate was formed on addition of acetic acid. The chief constituent of this precipitate appeared to be a nucleoprotein. The leucocytes, on treatment with acid, yielded a trypsin-like ferment, which could digest fibrin in presence of alkali. Pepsin was not found. Diastase was present, but not lipases. The leucocyte extract exerted a rennet-like action, and also clotted goose-plasma; a laccase could also be detected, but not a glycolytic ferment. The leucocytes exerted an antihæmolytic action on saponin and tetanus toxin, although no antitétanic action could be detected in experiments on animals. S. B. S.

**The Biology of the Phagocytes. VII. The Influence of Calcium Ions on Chemiotaxis.** HARTOG J. HAMBURGER (Biochem. Zeitsch., 1910, 23, 66-84).—It was shown by the two following methods that calcium ions promote chemiotaxis: (a) Capillary tubes with calcium-free and calcium-containing cultures were introduced under the skin of rabbits, and the length of the column of leucocytes entering the tubes was measured; (b) calcium-containing and calcium-free saline were introduced into the rectum of different rabbits, and then the length of the leucocyte column was measured which was formed when capillary tubes of bacterial cultures were introduced under the skin. Experiments were also carried out in a similar way with filtrates from bacterial cultures. In all cases, calcium salts stimulated the activity of the phagocytes. Calcium-containing natural mineral waters also stimulate phagocytes. S. B. S.

**Haemolysis by Lipoids.** H. LIEFMANN and MICHAEL COHN (Biochem. Zeitsch., 1910, 23, 85-115).—Haemolysis by lecithin or cholesterol is not appreciably affected by the addition of immune sera (rabbit immunised against sheep's blood) when the latter is added in weak concentration; haemolysis by soaps, on the other hand,

is delayed. Probably the inhibition by protein plays a rôle as well as the specific receptor action. Hemolysis by lecithin is inhibited by small amounts of cholesterol; hemolysis by oleic acid and soaps, on the other hand, is only slightly inhibited by relatively large quantities of this substance. The "albumin" fraction of guinea pigs serum ("end piece" of the complement) binds soap, lecithin, and oleic acid, whereas the "globulin" fraction ("middles piece") hinders soaps strongly, lecithin not appreciably, and oleic acid not at all. Furthermore, in cases of immediate total hemolysis by addition of hemolytic lipoids, and subsequent addition of serum, the latter can be replaced by "albumin," but not by "globulin." In the case of hemolysis by commercial lecithin preparations, it is not only the impurities, but the lecithin itself, which plays a part. S. B. S.

**The Residual Carbon of the Blood.** STEFANO MANCINI (*Biochem. Zeitsch.*, 1910, 23, 149-156).—By "residual carbon" is meant that amount of carbon which remains in the blood after precipitation of the protein contents by phosphotungstic acid. It was determined by Messinger's method of oxidation by acid dichromate mixture. The amount found in blood of the same species was approximately constant (mean 0.780 gram in 100 c.c. of blood). No great deviations were observed, however, in blood of different species of animals (variations from 0.0756 to 0.0844 gram per 100 c.c. blood). By keeping the blood cool for twenty-four hours, no marked changes in this amount were observed. About half the residual carbon is in the form of sugar (analysis by Pflüger's method). The quantity of residual carbon increases after loss of blood, and after ligation of the kidney vessels and ureters. It also increases after gradual phosphorus poisoning. S. B. S.

**A New Form of Blood gas Pump.** GEORGE A. BUCKMASTER and JOHN A. GARDNER (*J. Physiol.*, 1910, 40, 373-377).—The apparatus described and figured is a modified Toepler pump. The main improvement is the entire absence of taps and joints, and, consequently, of leakage. W. D. H.

**Lipase.** HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, *J. Biol. Chem.*, 1910, 7, xvii-xviii).—The amount of human pancreatic lipase determines the extent of digestion, that is, the point of final equilibrium between the triolein and the products of its hydrolysis. When lipase is abundant, digestion is practically complete; when triolein is relatively abundant, the percentage hydrolysis is small, although the actual amount of acid liberated may be considerable. W. D. H.

**The Nutritive Value of Some Soluble Pentosans, Mannans, Levulans, and Galactans.** MARY DAVIES SWARTZ (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xlii-xlv).—Galactans are not appreciably affected by any of the micro-organisms used; pentosans, mannans, and levulans are gradually decomposed by soil and faecal anaerobes. When introduced parenterally they are not

retained or altered by the organism, but are gradually excreted in the urine. Those hemicelluloses which are most readily attacked by bacteria disappear most completely from the alimentary tract (man or dog). There is no justification for considering these carbohydrates as of any appreciable nutritive value.

W. D. H.

**Gastric and Peptic Digestion of Fibrin. Variations of the Ratio Fibrin/Hydrochloric Acid Solution.** EUGENE CHOAY (*J. Pharm. Chim.*, 1910, [vii], 1, 521—528).—In the previous paper (this vol., ii, 516) the variation of the ratio  $F/G$  or  $P$ , where  $F$  is dry pork fibrin,  $G$  a dry extract of the stomach membrane of the pig, and  $P$  commercial pepsin, was investigated under conditions in which the ratio of the fibrin to dilute hydrochloric acid (0.25%) remained constant. In the present paper the effects due to variation of the latter ratio are considered. The hydrochloric acid used was of 0.25% strength throughout the experiments, and two ratios  $F/HCl$  solution were investigated, namely, 2.5/60 and 2.5/120. The ratios  $F/G$  or  $P$  used were 6.25/1, 25/1, and 1000/1. The determinations made were those suggested previously. The results, which are tabulated in detail in the original, show that under these conditions dilution quickens the dissolving power of considerable quantities, but slows the activity of moderate and small quantities of the gastric ferments, and that under all conditions total gastric extract is more active than pepsin.

T. A. H.

**The Catabolism of Methylated Xanthines.** JULIUS SCHMID (*Zeitsch. physiol. Chem.*, 1910, 67, 155—160).—The fate of methylated xanthines is of interest, as they occur in tea, coffee, and cocoa. Previous work has shown that 20—50% appear in the urine as mono-methylxanthine, some leaves the body unchanged, and a part is oxidised to an unknown end product in which the purine ring is broken down. The question investigated in the present research is, in what organ does the change occur, and experiments were performed *in vitro* with minced organs and tissues. Blood, liver, kidney, spleen, lung, and muscle were used; all produce the effect to about the same degree.

W. D. H.

**Purine Metabolism in Hibernating Animals.** ERNEST L. KENNAWAY (*Bio. Chem. J.*, 1910, 5, 188—191).—Dormice, when awaking from hibernation, were found to contain 30% more purine nitrogen than was present before or during hibernation. The results indicate that a synthesis of purines takes place at the time of awakening.

W. D. H.

**Repeated Fasting.** PAUL E. HOWE and PHILIP B. HAWK. **Fasting Studies on Men and Dogs.** P. E. HOWE, H. A. MATHILL, and P. B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xlv, xlvii—xlviii).—A second fast, following a first of fifteen days, lasted twice as long. There was a more gradual loss of weight in the dogs, a much lower and more constant nitrogen output, a slight rise in ammonia, and a more gradual drop in

the creatine excreted, but this was followed in both fasts by a rise towards the end. The loss in body-weight was 45.8% in the first, and 46.8 in the second fast.

In the second paper further, experiments of the same kind are recorded, one dog fasting for one hundred and seventeen days, the longest on record; it was carefully fed back to health and started on a second fast. The men fasted seven days, and lost 7.7% of weight. Details are given of the composition of the urine, particular attention being paid to creatine and creatinine.

W. D. H.

**Occasional Occurrence of Urobilin in Gastric Juice.** PIERRE LAVIALLE (*Chem. Zentr.*, 1910, 1, 1732; from *Bull. Sci. Pharmacol.*, 1910, 17, 105—107).—In three cases urobilin was detected in the gastric juice of invalids, being formed, in the author's opinion, by bacterial reduction of the bile pigment which passed from the duodenum to the stomach. The gastric juice did not show Gmelin's reaction.

E. J. R.

**The Nitrogen Balance in Pregnant Dogs.** JOHN R. MURLIN. **The Protein Metabolism of Parturient Women.** J. R. MURLIN and THORNE M. CAAPESTER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, x, xlix).—The amount of nitrogen lost is not greater in the early weeks of gestation than it is in complete sexual rest. In the menstrual period, there is marked retention of nitrogen.

The urine in women during the last few weeks of pregnancy and the puerperium shows the usual parallelism between total nitrogen and sulphur. Just previous to parturition, there was in one case a rise in creatine excretion. The creatine is also high during the puerperium, whilst involution of the uterus is occurring.

W. D. H.

**Pentose in the Pancreas.** WALTER A. JACOBS and PHOEBUS A. LEVENE (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, ix).—The only pentose occurring in the nucleo-proteins of the pancreas and liver is *d*-ribose.

W. D. H.

**Action of Bile and Bile Salts on the Tonus of Automatic Movements of the Intestine.** G. D'ERRICO (*Zeitsch. Biol.*, 1910, 54, 286—298).—Bile or bile salts added to Ringer's fluid lower the tonus of the intestine (large and small) of the cat, and its rhythmical movements are diminished.

W. D. H.

**Lipoids. XI. Comparative Chemistry of the Brain.** SIGMUND FRÄNKEL and KURT LINNEAT (*Biochem. Zeitsch.*, 1910, 23, 44—52).—Brain substance from various animals, and from different parts of the human brain (cortex, medulla, medulla oblongata, cerebellum, etc.), was submitted to analysis by the following method: The brain, made into a paste, was either dried to constant weight or treated first with warm acetone and then with hot acetone, the extracts mixed, and the amount extracted and the residue weighed. By either

... methods the amount of water could be ascertained. The dried substance was then extracted successively in a Soxhlet apparatus with petroleum, low boiling petroleum, benzene, absolute alcohol, and 80% alcohol. The amount extracted by these solvents was thus estimated, and the results expressed in percentages of fresh brain, dried brain, and total lipoids. Considerable variations were found in the different samples analysed, and the authors give their results in tabular form.

S. B. S.

**The Place of Formation of Uramic Acids.** PETER PHILIPSONOFF (*Biochem. Zeitsch.*, 1910, 28, 131—139).—The investigations were undertaken with the object of throwing light on the mechanism of urea formation in the body, and of testing Hofmeister's hypothesis of the formation of this substance by the oxidative synthesis of ammonia with an amino-acid residue. When ox-blood containing taurine was perfused through ox-liver, no taurocarbamic acid could be detected; if, however, a mixture of taurine and glycine were added to the blood, the carbamic acid could be detected after perfusion. The acid was not in this case isolated in a crystalline form, but its presence was determined by the isolation of its acid products of hydrolysis. The author gives full experimental details as to the methods of isolation of taurocarbamic acids from animal fluids.

S. B. S.

**A Reducing Endo-enzyme in Liver and Kidney.** DAVID FRASER HARRIS (*Bio-Chem. J.*, 1910, 5, 143—160).—A full account of a research previously published (this vol., ii, 324).

W. D. H.

**Heat Production of Muscle.** A. V. HILL (*J. Physiol.*, 1910, 40, 389—403).—The heat production during the twitch of a frog's muscle lasts a very short time normally; if it lasts longer (several minutes), "contracture" is present. Normal saline solution increases the "tone," but if the amount of contraction is the same as in the absence of the increased tone, heat production is decreased. The view is advanced that the heart is analogous to a muscle stimulated at regular intervals; if this is so, the tonic condition of the heart involves far less energy breakdown than the condition in which the heart beats from complete diastole.

W. D. H.

**The Relationship between Muscular Rigor and Protein Coagulation; Chemical Stimulation of Muscle.** I. EMMET ROSS (*Zeitsch. Biol.*, 1910, 54, 299—328).—After the action of ammonia gas, the frog's skeletal muscles lose the capacity to undergo rigor under the influence of chloroform and ether. Ammonia, however, has no influence if applied subsequent to the rigor produced by chloroform or ether. Certain differences in the action of ammonia are noted in relation to concentration and temperature. In the early stage of chloroform and ammonia rigor, the muscle recovers its irritability on removal of the reagent. In later stages this is not so. In hyperammonia solution the sensitiveness of muscle to chloroform is increased; in isotonic eucrose solution it is lessened.

W. D. H.

**Do Muscle and Blood-serum contain Creatinine?** PHILIP A. SHASTAL and A. R. KINOS (Proc. Amer. Soc. Biol. Chem., 1909; *J. Biol. Chem.*, 1910, 7, xxx).—Fresh dog's muscle and dog's blood-serum contain respectively 1–6 mg. and 1 mg. of creatinine. The view that creatinine arises in muscle tissue is supported. W. D. H.

**Phosphorus in Beef.** C. K. FRANCIS and PERRY F. TROWBRIDGE (*J. Biol. Chem.*, 1910, 7, 481–501).—Any method which involves heating of the solution before precipitation of inorganic phosphorus gives incorrect results, as organic compounds are converted into inorganic by heat. From 52 to 65% of the total phosphorus in cold-water extracts of beef is in the organic form; this may be reduced to from 9 to 20% by heating to 70°. The round of beef contains more phosphorus soluble in cold water than any other cut. It is found chiefly in the muscular and connective tissues; the fat contains but little. The flesh of a thin animal contains more soluble phosphorus than that of a fat animal. W. D. H.

**Purine Enzymes of Guinea Pig and Rabbit.** PHILIP H. MITCHELL (Proc. Amer. Soc. Biol. Chem., 1909; *J. Biol. Chem.*, 1910, 7, xi).—The purine enzymes in the two animals are the same; this suggests the possibility that the relationship of species may be indicated by the distribution of these enzymes. W. D. H.

**Colour Change in the Isopod, *Ligia oceanica*.** JOHN TAYLOR (Proc. physiol. Soc., 1910, xi–xli; *J. Physiol.*, 40).—The colour changes in the surface of this animal are due to chromatophores, but their stimulation by light is indirect, the eye being the receptor organ. W. D. H.

**Manganese in Fresh-water Mussels.** HAROLD C. BRADLEY (Proc. Amer. Soc. Biol. Chem., 1909; *J. Biol. Chem.*, 1910, 7, xxxvi–xxxvii).—Manganese can be detected in most of the organs of the fresh-water mussel, and is most abundant in the gills and mantle. The eggs and embryo also contain it. The source of the element is the food of the animals, crenothrix and diatoms, which are able to concentrate manganese from its very dilute solution in the water. In lakes where the water is very pure, neither crenothrix nor mussel are found. The manganese probably has a respiratory function in the tissues and blood of these lamellibranchs. W. D. H.

**The Behaviour of Nucleic Acid in the Cleavage of the Sea-urchin's Egg.** ERNST MASING (*Zeitsch. physiol. Chem.*, 1910, 67, 161–173).—The nucleic acid in the fertilised egg of the sea-urchin does not increase as cell division goes on; although the mass of the nuclei may be increased a hundred fold, the amount of nucleic acid is hardly raised at all. Nucleic acid and the chromatin of histologist cannot, therefore, be identical. W. D. H.

**Is Bence-Jones' Protein Produced from Osseo-albumoid?** JACOB ROSENBLUM (Proc. Amer. Soc. Biol. Chem., 1909; *J. Biol. Chem.*, 1910, xiv–xvi).—Some of the results in the urine after admin-



starting digested osseo-albumoid either by the mouth or under the skin indicate that Benoit-Jones' protein may be formed from osseo-albumoid by the action of enzymes in the bone marrow; but this view is put forward with considerable reserve.

W. D. H.

**The Presence of Insoluble Salts of Calcium (Oxalate and Phosphate) in Renal Calculi in Large Amount in a Preponderating Number of Cases, and the Bearing of this Finding on Calcium Metabolism in Gout and Allied Conditions.** W. W. MACKARELL, BENJAMIN MOONE, and W. THELWALL THOMAS (*Bio-Chem. J.*, 1910, 5, 161—180).—Analyses of a number of renal calculi are given which bear out the statement contained in the title. There is no hope of dissolving such stones by lessening the alkalinity of the blood, for even when powdered they dissolve very slowly even in 1 in 4 hydrochloric acid. Anti-acid treatment, however, such as is employed in gout, would probably lead to more rapid growth of such calculi.

W. D. H.

**Elimination of Nitrogenous Waste during Renal Excretion in the Starving Subject. Relation of this Elimination to that of Water, the Vehicle for Urinary Excreta. Independence of the Two Phenomena.** AUGUSTE CHAUVEAU and CH. CONTRERAN (*Compt. rend.*, 1910, 150, 1647—1652. Compare *ibid.*, 1478).—A series of experiments were carried out on dogs in a state of starvation. The urine was measured at regular intervals, and the total nitrogen estimated. At the commencement of the last period in each series, a considerable bulk of water was introduced into the system through the stomach or per rectum. No definite proportionality was observed between the volume of water eliminated and the amount of nitrogen. The authors consider that variations in the amount of urine excreted do not seriously affect the conclusions to be drawn from metabolism experiments. Even in experiments of short duration, the renal excretion of nitrogenous material remains a trustworthy index of the extent of protein degradation.

W. O. W.

**Glycuronic Acid and Ethereal Sulphates in Human Urine.** CARL TOLLENS (*Zeitsch. physiol. Chem.*, 1910, 67, 138—154).—A healthy man excretes as a rule twice as much glycuronic acid as ethereal sulphates (0.35:0.18 gram), but the former substance may rise considerably without being a pathological sign. Indole given by the mouth unites mainly with sulphuric acid, phenol with glycuronic acid. The two substances, as a rule, rise and fall together, usually but not always proportionally to the amount of intestinal putrefaction. In peritonitis and enteritis there is a marked increase in both. The same is true in cresol poisoning.

W. D. H.

**The Urine in Eclampsia.** LYMAN B. STOOKEY (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, 1).—In eclamptic urine (five cases) the urea nitrogen is low; the ammonia nitrogen and mono-amino-acid nitrogen are both high. There was also a positive p-dimethylaminobenzaldehyde reaction. Washing out the colour with a

weak antiseptic solution and a low protein dietary lessened these peculiarities and also the clinical signs. In two cases a similar result followed the administration of iodides and thyroid. W. D. H.

**On the So-called Thermo-soluble Protein of Bence-Jones.** A. CHRISTIANS, AIME GÉRARD, and C. THOMAS (*J. Pharm. Chim.*, 1910, [vii], 1, 582—585).—The urine of a patient suffering from albuminuria was examined several times during some months. The urine constantly gave the Bence-Jones reaction, but the earlier specimens when half saturated with sodium chloride did not lose their thermo-solubility entirely, whilst in later specimens similar treatment caused the thermo-solubility to disappear completely. Dextrose, biliary pigments, and urobilin were absent. Under the microscope, numerous granular hyaline cylinders were observed as well as epithelial cells of renal origin. A litre of the urine contained 2·61 grams of serin and 0·08 gram of globulin. The results confirm Grimbert's opinion that the Bence-Jones reaction is not that of a specific protein, but is given by many of these substances (compare Abstr., 1908, ii, 212; Gascard and Devalmont, *ibid.*, ii, 519). T. A. H.

**A Case of Alcaptonuria.** A. RAVOLD and WILLIAM H. WARREN (*J. Biol. Chem.*, 1910, 7, 465—480).—A case of this comparatively rare condition is described with full clinical details. The analysis of the urine, including the separation and identification of homogentisic acid, is also described in full. No new feature of importance appears to be noted. W. D. H.

**The Behaviour of *p*-Aminophenylalanine in Alcaptonuria.** LEON BLUM (*Zeitsch. physiol. Chem.*, 1910, 87, 192—193).—Abderhalden and Massini (this vol., ii, 638) found that *p*-amino-tyrosine increases the excretion of homogentisic acid in alcaptonuria, or rather that the reducing power of the urine is increased. In the present research, *p*-aminophenylalanine was given to one of these patients; there was a small rise in the homogentisic acid of the urine, but it is too small to indicate with certainty the transformation of one substance into the other. W. D. H.

**The Amount of Cholesterol and Cholesterol Esters in the Normal and Atheromatous Aorta.** ADOLF WINDAUS (*Zeitsch. physiol. Chem.*, 1910, 87, 174—176).—The amount of free cholesterol and still more so that of cholesterol esters is increased in atheromatous as compared with normal aorta.

The figures given are :

	Free cholesterol.	Cholesterol as ester.
1. Normal aorta .....	0·119%	0·047%
2. " " .....	0·103%	0·032%
3. Atheromatous aorta...	0·741%	1·053%
4. " " " ..	0·673%	0·792%

W. D. H.

**Lactic Acid in Diabetes.** JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1910, li—lii; *J. Physiol.*, 40).—One hundred to two hundred and fifty

etc. of the urine are rendered slightly alkaline with sodium carbonate, evaporated, and extracted with alcohol. The extract is evaporated to a syrup, and strongly acidified with phosphoric acid. The ether soluble acids are then transferred to dilute sodium carbonate solution by shaking ether alternately with the syrup and sodium carbonate solution. This solution is then evaporated to dryness, and the lactic acid in it estimated by the author's distillation method. The normal excretion of lactic acid is less than 0.02 gram per diem. In diabetes it rises to 0.05—0.6. After an abundant meal of carbohydrates, the lactic acid rises to five times the normal amount. In both cases the lactic acid therefore probably originates from a partial conversion of the sugar of the blood into the acid. Lactates given by the mouth increase the lactic acid in the urine; the retention of, and presumably the ability to use, lactic acid is not much less in the diabetic than in the normal person.

W. D. H.

**Deterioration of Diphtheria Antitoxin.** EDWIN J. BANZHAF (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xiv-xvii).—The amount of deterioration was determined under various conditions; the deterioration of antitoxic citrated plasma was extremely low, even at room temperature.

W. D. H.

**Gastrotoxin and the Healing of Gastrotoxic Ulcers.** CHARLES BOLTON (*J. Path. Bact.*, 1910, 14, 418—431).—Gastrotoxic serum may be obtained by immunising animals (rabbits) with rabbits' gastric cells. The ulcers produced are due to self-digestion. They heal in a few weeks whatever the acidity of the juice may be. A sloughing ulcer lowers the acidity, but during healing the acidity is normal. Hyperacidity occasionally occurs.

If the stomach movements are normal, neither *Bacillus pyocyaneus* nor *B. coli communis* are able to delay the healing process.

W. D. H.

**Cell-Proliferation.** CHARLES POWELL WHITE (*J. Path. Bact.*, 1910, 14, 450—462).—Aseptic abscesses formed by the subcutaneous injection of turpentine or higher fatty acids become lined with squamous epithelium; the same is true for injections into the mammary gland, but an epithelial lining does not form unless the ulcers come into contact with epithelium. The endothelium in the neighbourhood also proliferates, and this is regarded as a phagocytic reaction. The experiments do not afford any evidence in favour of a direct formative irritant.

W. D. H.

**Physiological Action of the Sulphurous Acid Contained in White Wines.** JEAN GAUTRELET (*Ann. Falsif.*, 1910, 3, 226—235).—The results are recorded of a considerable number of experiments in which dogs and men received food and wine containing sulphurous acid; the administration of the latter was continuous for some length of time after the subjects had been kept under observation during a fore-period. The investigation was carried out by a Commission; the general conclusion, arrived at from a consideration of the effects

observed, is that sulphurous acid, in quantities up to 400 mg. per litre of wine, is not injurious to health, even when one-fourth of the quantity of acid just mentioned is present in the free state in the wine.

W. P. S.

**Anæsthetics.** AUGUSTUS D. WALLER, F. W. HEWITT, and SIR FREDERICK TREVES (*Brit. Assoc. Report*, 1909, 296—315).—The report deals with the Routine Use of a Mixture of Chloroform and Ether [with JOSEPH BLUMFELD], a description of the Chloroform Balance, the Physiological Effects of Mixed Anæsthetics, the Comparative Action on Isolated Muscle of Alcohol, Ether, and Chloroform, the Percentage of Chloroform in the Blood of Anæsthetised Animals and of Man under Various Conditions [with JOHN A. GARDNER and BUCKMASTER], and the Comparative Power of Chloroform, Ether, and Alcohol gauged by Intravenous Injection [with W. L. SYMES].

E. H.

**Products of the Decomposition of Chloroform in the Organism.** MAURICE NICLOUX (*Compt. rend.*, 1910, 150, 1777—1778. Compare this vol., ii, 637).—Desgrez has signalled the decomposition of chloroform into carbon monoxide and water under the influence of aqueous alkalis (*Abstr.*, 1898, i, 166; ii, 530). This decomposition proceeds rapidly when chloroform and sodium hydroxide are present in aqueous solution in the same concentration as they occur in blood during anæsthesia. It has been shown by experiments on dogs that the same reaction occurs in blood. No formates were detected in the urine during anæsthesia.

W. O. W.

**Physiological Action of Choline.** LAFAYETTE B. MENDEL and FRANK P. UNDERHILL (*Zentr. Physiol.*, 1910, 24, 251—253).—The greatest possible care was taken in the preparation of choline in a state of purity. The uniform result in anæsthetised, but not curarised, cats of intravenous injection was a temporary fall of blood-pressure, which does not occur after atropinisation. The original statements of Halliburton and Mott are thus confirmed. The contrary results described by Modrakowski could not be repeated (compare Abderhalden and Müller, this vol., ii, 530).

W. D. H.

**Caffeine Glycosuria.** WILLIAM SALANT and G. W. KNIGHT (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, lii—liii).—In rabbits, glycosuria follows administration of caffeine within two or three hours, and lasts several, but not more than twenty-four, hours. The dose required is larger when given by the mouth. The effective dose is smaller when the diet is rich in carbohydrates, or when calcium chloride is also injected. Calcium chloride in itself produces no glycosuria. Similar experiments on dogs gave negative results.

W. D. H.

**The Cardio-vascular Action of Green Coffee Compared with that of Corresponding Doses of Caffeine.** V. PACHON and EM. FERROT (*Compt. rend.*, 1910, 150, 1703—1705).—The authors have

examined the physiological action of an extract of green coffee, in which the enzyme has been destroyed by alcohol. With dogs, intravenous injection caused marked lowering of the blood-pressure, followed by a gradual rise, and a diminution in the volume of the kidney. The administration of atropine did not influence these symptoms. Corresponding doses of pure caffeine produced no apparent effects.

W. O. W.

**The Presence in Ergot and Physiological Activity of  $\beta$ -Iminazoylethylamine.** GEORGE BARGER and HENRY H. DALE (*Proc. physiol. Soc.*, 1910, xxxviii—xl; *J. Physiol.*, 40).—The specific action on the cat's uterus produced by ergot is due to a base which was identified with  $\beta$ -iminazoylethylamine. This originates from histidine by the splitting off of carbon dioxide.

W. D. H.

**Action of Peptone Intravenously Injected in the Guinea Pig.** A. BIEHL and R. KRAUS (*Zentr. Physiol.*, 1910, 24, 258—261).—Peptone injection is toxic to the guinea-pig, the most marked result being spasm of the bronchial muscles. In dogs the effect is mainly paralysis of the smooth muscles, especially in the abdominal sympathetic area. The bronchial muscles are innervated by the vagus. The symptoms in the guinea pig are extremely similar to those seen in anaphylaxis.

W. D. H.

**The Effect of Inanition and of Various Diets on the Resistance of Animals to Certain Poisons.** REID HUNT (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxix—xxx).—Marked variations occur in the resistance of mice, rats, guinea pigs, and dogs when fed on different diets, the poisons being morphine, cocaine, and acetonitrile. In extreme cases, the lethal dose was raised thirty times. These results are not due to the proportion of fats, carbohydrates, and proteins, but to specific effects of the foods. In one case, for example (the increased resistance of mice fed on oatmeal to acetonitrile), the effect seems to be due to the stimulation of growth in the thyroid which is produced by some substance in oatmeal. In some cases a restricted diet increased resistance.

W. D. H.

**Poisons and Enzymes.** HUBERT W. BYWATERS and AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xlv—xlvii; *J. Physiol.*, 40).—The suggestion has been made that the effect of certain alkaloids on muscle may be due to their action on enzymes. Aconitine, however, was found to have no action on ptyalin, and only a slight retarding action on invertase.

W. D. H.

**Serological Studies by means of the "Optical Method."** X. EMIL ABDERHALDEN and LUDWIG PINCUSOHN (*Zeitsch. physiol. Chem.*, 1910, 63, 83—105).—The authors have investigated the action of a large number of toxins (diphtheria, pyocyanase, ricin, cobra-toxin, etc.) and also of various sera, both normal and from animals undergoing immunisation, on different peptones, with the object of determining the activity of ferments. The changes of rotation were measured, and the results are plotted on thirty-seven plates.

S. B. S.

## Chemistry of Vegetable Physiology and Agriculture.

**The Growth of Various Species of Bacteria and other Micro-organisms in Atmospheres Enriched with Oxygen.** BENJAMIN MOORE and R. STENHOUSE WILLIAMS (*Bio.-Chem. J.*, 1910, 6, 181—187).—Twenty-six varieties of organism were subjected to experiment; two of them, namely, those of tuberculosis and plague, stand out prominently as oxyphobic; the *Staphylococcus* growths were also adversely affected by increase of oxygen. The tubercle bacillus was killed by three weeks' exposure to a higher percentage of oxygen. The bacillus of plague was not killed by a few days' exposure to an oxygen percentage of from 60 to 90, but growth was arrested; longer times were not tried.

W. D. H.

**Utilisation of Amino-acids and Polypeptones by the Tubercle Bacillus.** WILLIAM F. KOELKER and B. W. HAMMER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, li—lii).—Various amino-acid were added to the culture medium; there seems to be a difference in the behaviour of the homologous and the methyl-substituted amino-acids; thus glycine and alanine are favourable to the growth of the tubercle bacillus; aminoisobutyric acid, valine, and leucine give no growth. The investigation with polypeptides is to be continued.

W. D. H.

**Chemical Reactions Occurring during Alcoholic Fermentation. IV.** EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1910, 43, 1773—1795. Compare Abstr., 1904, ii, 199; 1905, ii, 274; 1906, ii, 790).—Lactic acid has been regarded as an intermediate product of alcoholic fermentation, partly owing to its appearance during fermentation with pressed yeast-juice. It was shown by Pasteur originally, and the fact has repeatedly been confirmed since, that lactic acid is never produced during fermentation with a pure living yeast.

As the result of a systematic and careful study of the behaviour of lactic acid towards living yeast, it is now shown that it is neither fermented nor produced during fermentation (compare Sator, *Trans.*, 1906, 89, 141; 1908, 93, 231). Accordingly, the hypothesis that lactic acid is an intermediate product of fermentation is abandoned.

Methylglyoxal is not fermented either by living yeast or pressed yeast juice, neither can its formation be detected during the fermentation of sugar. Pure glyceraldehyde is slowly fermented by yeast to the extent of 10—25%. W. Löb (*Zeitsch. Elektrochem.*, 1907, 13, 511) was unable to detect it as a product of fermentation. Dihydroxy-acetone (compare Bertrand, Abstr., 1904, ii, 760) is fermented by pressed yeast juice in presence of sodium chloride to the extent of 80—90%. With living yeast, about 50% was fermented in twenty-four hours. Boysen-Jensen (Abstr., 1909, ii, 172) claims to have detected the formation of dihydroxyacetone during fermentation. The hypo-

It is advanced that dihydroxyacetone is to be regarded as the intermediate product of fermentation.

Glycerol is produced during fermentation with pressed yeast juice at the cost of the dextrose fermented, and is not formed from proteins or nucleic substances (compare Ehrlich, *Biochem. Zeitsch.*, 1909, 18, 423).

Ethylideneoxyformate is not fermented by pressed yeast juice. A similar negative result is obtained with  $\alpha$ -glucoheptose.

Sterilised 10% dextrose solution, preserved at the ordinary temperature for five years in sealed tubes, was found to have remained unchanged.

E. F. A.

**Formation of Acetaldehyde in Bitter Wines.** E. VOISENET (*Compt. rend.*, 1910, 150, 1614—1616).—Acetaldehyde gives a bluish-green coloration with a solution of albumin containing hydrochloric and nitrous acids (Abstr., 1905, ii, 59; this vol., ii, 466). By applying this test, with others, acetaldehyde has been detected in the distillate from bitter wines, and shown to be absent in that from normal wine. The aldehyde appears to be formed from the glycerol of wine, since it is produced when the bacteria causing bitterness are cultivated in an artificial medium containing 1% of glycerol.

W. O. W.

**The Production of Volatile Fatty Acids and Esters in Cheddar Cheese, and their Relation to the Development of Flavour.** S. K. SUZUKI, E. G. HASTINGS, and EDWIN B. HART (*J. Biol. Chem.*, 1910, 7, 431—458).—Lactose disappears from Cheddar cheese in from three to six days; the lactic acid increases, and this increase after the disappearance of the lactose is probably of protein origin. The usual form of lactic acid is racemic. However, lactose solutions inoculated with *B. lactis acidii* produce the active acid, or when inoculated with a piece of the cheese a mixture of active and inactive acids is produced. No enzyme capable of producing lactic or volatile fatty acids from lactose could be isolated. Certain organisms in lactose solutions yield not lactic, but volatile fatty acids instead; the latter are also formed in the ripening of the cheese after lactose has disappeared; acetic, propionic, butyric, hexoic, but not valeric, acid were found. Formic acid was only found at the five and a-half months' stage. The principal sources of acetic and propionic acids are probably lactates; traces may come from protein or glycerol. The butyric and hexoic acids come from fats and proteins. The distillate ("flavour" solution) contained alcohols and esters; in mild cheeses these were mainly ethyl alcohol and ethyl acetate; in pungent cheeses mainly ethyl esters of hexoic and butyric acids. Succinic acid was also identified.

W. D. H.

**Influence of Humus on the Decomposition of Urea.** HARALD R. CHRISTENSEN (*Centr. Bakt. Par.*, 1910, ii, 27, 336—362).—Addition of a small amount of soil extract to a solution of urea containing the usual minerals failed to induce a production of ammonia, whilst the further addition of a little potassium humate soon caused a vigorous liberation of ammonia from the urea. Artificial humic acid from sucrose has a similar effect. Dextrose and various other non-nitrogenous carbon compounds give rise to ammonia production when

added to crude culture of urea bacteria. With pure cultivations these substances (with the exception of calcium lactate) are only very slightly utilised, if at all.

Asparagine, and especially peptone, induce a vigorous production of ammonia when added to pure culture of urea bacteria containing urea.

Solutions of urea containing no other carbon compound are readily decomposed with production of ammonia when inoculated from a fermented humin-urea solution.

N. H. J. M.

**Action of Ultra-violet Rays on (I) Certain Solutions Used in Pharmacy; (II) Certain Fatty Substances, Glucosides, Alkaloids, and Phenols.** ANDRÉ LESURE (*J. Pharm. Chim.*, 1910, [vii], 1, 569—575, 575—576).—The object of this work was primarily to ascertain whether the sterilising action of ultra-violet rays could be used in rendering medicinal preparations, particularly those used for injection subcutaneously or otherwise, aseptic. Twenty-four different liquids were exposed during one to five minutes or fifteen to thirty minutes to the light emitted by a Cooper-Hewitt mercury lamp. The permeability to the rays was observed by their effect on sensitised paper after passing through the solution under observation. In most cases the permeability was comparable to that of water, but for solutions of atoxyl, caffeine, eserine salicylate, apomorphine hydrochloride, gentiopicroin, or olive oil it was from 1/10 to 1/5th that in water. With solutions of mercuric iodide (in sodium iodide), quinine dihydrochloride, or quinine disulphate, it was practically nil.

Certain of the solutions showed some change, thus silver nitrate, eserine salicylate, apomorphine hydrochloride, and atoxyl all became coloured after five minutes' exposure, whilst morphine hydrochloride, arbutin, and guaiacyl cacodylate developed colour after an exposure of from fifteen to thirty minutes. Olive oil was decolourised after illumination during thirty minutes, but there was no marked change in the constants of the oil.

A solution of aucubin containing *Bacterium coli* was completely sterilised in thirty seconds, but a similar preparation of gentiopicroin was not completely sterilised after thirty minutes' exposure.

In a second series of experiments, it was found that olive oil became acid after exposure during one hour, and that aucubin and gentiopicroin were decomposed and yielded reducing products after three hours.

Arbutin became very much coloured after three hours' illumination, due to formation of quinol and oxidation of this. Methylarbutin behaved similarly, but required longer exposure before coloration occurred. Quinol became coloured in five minutes, but methylquinol only after thirty minutes, and the solutions were then less permeable to the rays. Cocaine hydrochloride and pilocarpine hydrochloride did not appear to be affected appreciably even after three and a-half hours, although the latter became slightly coloured.

T. A. H.

**Selective Antiseptic Action\* of Copper Salts.** ALFRED SPRINGER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxi—xxxii).—Copper salts are highly selective, being most



important in inhibiting the action of putrefactive organisms. This view is supported by some experiments on eggs, and the suggestion is made that the selective action may prove to be of therapeutic importance. W. D. H.

**Composition of the Seeds of Cultivated Plants.** ERNST SCHULZE (*Landw. Versuchs-Stat.*, 1910, 73, 35—170).—Results of analyses of seeds of various plants, including determinations of the proteins and other nitrogenous substances, constituents of ether extracts, soluble and insoluble carbohydrates, phosphorus compounds, and ash constituents.

The qualitative methods employed are described. N. H. J. M.

**Chemical Organisation of a Typical Fruit.** ALBERT E. VINSON (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xi—xli).—Unripe dates of the invert sugar type contain high percentages of sucrose so long as the fruit remains intact. The fresh juice also contains appreciable amounts of sucrose, but this is rapidly hydrolysed to invert sugar in the presence of the pulp; this is due to the fact that when the tissues are crushed the intracellular invertase comes into contact with the sucrose. When filtered, the diastase remains with the pulp, but as the pressure employed during filtration is increased, larger quantities of soluble nitrogenous cell constituents make their way into the filtrate. J. J. S.

**Ratio of Plant Nutrients as Affected by Harmful Soil Compounds.** OSWALD SCHREINER and J. J. SKINNER (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxiii—xxxiv).—As the result of numerous experiments made by growing plants with varying amounts of phosphate, nitrate, and potassium fertilisers, both in the presence and absence of dihydroxystearic acid, it has been proved that the dihydroxy-acid greatly inhibits the plant growth, and that the effect is most marked where the ratios of the three fertilisers are least suited for growth. It is less harmful when the fertiliser is mainly nitrogenous than when mainly phosphatic or potassic, and the effect is also associated with a higher nitrogen removal.

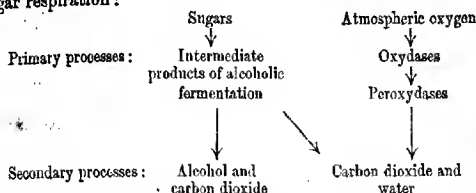
The amounts of potassium and phosphate removed were less in the presence of the dihydroxy-acid. J. J. S.

**The Mechanism of the Oxidation of Sugar in Plant Respiration.** S. KOSTYTSCHIEFF (*Zeitsch. physiol. Chem.*, 1910, 67, 116—137. Compare Abstr., 1909, i, 84, 173).—The readily oxidisable intermediate products formed during alcoholic fermentation can produce large quantities of carbon dioxide when treated with hydrogen peroxide and a ferrous salt. This was proved by using solutions which had been fermented by means of "hefanol," and were quite free from unaltered dextrose. As dextrose itself is readily oxidised by hydrogen peroxide and ferrous salts, it cannot be definitely stated, as the results of the above experiments, that zymase facilitates the oxidation of sugar. The same intermediate products also yield large quantities of carbon dioxide in the presence of hydrogen peroxide and

peroxydase from wheat seeds. Dextrose itself does not yield carbon dioxide under these conditions, and the intermediate products do not yield carbon dioxide with hydrogen peroxide alone. The preparations of oxydase also contain catalase, and the addition of hydrogen peroxide, not merely destroys the catalase, but also the peroxydase; the effects of the catalase are, however, largely negated by the addition of potassium phosphate.

This is the first case in which carbon dioxide has been obtained from vegetable products by means of vegetable oxidising ferments.

The following scheme gives the main processes in the case of sugar respiration:



(compare Palladin, Abstr., 1909, ii, 511). The peroxydase functions as an inductor, and not as a catalyst. J. J. S.

**Concurrent Oxidising and Reducing Power of Roots.** OSWALD SCHREINER and MICHAEL X. SULLIVAN (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxii—xxxiii).—The roots of growing plants (such as wheat) can oxidise  $\alpha$ -naphthylamine, benzidine, phenolphthalein, aloin, etc., and the oxidation is the most marked where the growth is greatest. Wheat roots grown in a solution of sodium selenite neutralised by hydrochloric acid, reduce the selenite, producing a pink deposit of selenium on the root; the reaction is most marked where the growth is vigorous. Roots killed by immersion in boiling water show no reducing action, and no reduction takes place in an alkaline selenite solution. In the main, with increased oxidising power, there is an increase in the reduction, whilst certain concentrations of potassium iodide retard oxidation, but either increase the reduction or have no effect. J. J. S.

**Anæsthetics and Laurel Leaves.** AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xlix—li; *J. Physiol.*, 40).—In chloroform vapour there is the greatest evolution of hydrogen cyanide, in ether less, in alcohol less still; in water there is none. The decline in electrical response follows the same order, being greatest in chloroform; in water there is no response. The evolution of the poison is a post mortem sign, and the enzyme that produces it may remain active for days in spite of the anæsthetic which kills the protoplasm. W. D. H.

**Utilisation of Tricalcium Phosphate by Cruciferous Plants.** CIRO RAVENNA and M. ZAKORANI (*Biol. Zentr.*, 1910, 39, 495—496; from *Staz. sper. agrar. ital.*, 1909, 42, 389).—Pot experiments in which mustard, vetches, and oats were grown in sand

manured with mono- and tri-calcium phosphate respectively in addition to other salts. In the case of mustard, the fresh produce was almost the same with tricalcium phosphate as with the monocalcium salt, whilst with vetches, and especially oats, there was less fresh produce with tricalcium phosphate. The dry matter results show that the greatest difference was with mustard, whilst the percentages of ash in the dry matter and of phosphoric acid in the ash were, like the fresh produce, almost the same with the two manures in the case of mustard, but distinctly lower as regards ash, and very much lower as regards phosphoric acid, with vetches and oats grown with tricalcium as compared with monocalcium phosphate.

N. H. J. M.

The Action of Potassium Salts on the Formation of Sucrose in Seeds. G. DE PLATO (*Chem. Zentr.*, 1910, i, 1623; from *Staz. sper. agrar. ital.*, 1910, 43, 97—104).—The author examined peas grown on different soils, and found that those coming from soils rich in calcium and potassium compounds contained in comparison with others from soils deficient in these constituents more carbohydrate, particularly sucrose, more potassium, calcium, and magnesium, but less nitrogenous substance. It appears that potassium favourably influences the production of carbohydrate, magnesium its transportation and storage in the seed, and calcium the formation of salts of organic acids. These are the three chief factors determining the high proportion of sugar in peas.

E. J. R.

Presence of a Glucoside in the Leaves of the Pear Tree and its Extraction. ÉMILE BOURQUELOT and Mlle. A. FICHTEHOLZ (*Compt. rend.*, 1910, 151, 81—84. Compare Rivière, Abstr., 1904, ii, 583).—Pear tree leaves contain a glucoside which is easily extracted by ethyl acetate, the yield amounting to 1.2—1.4%. The substance has m. p. 194—195°,  $[\alpha]_D -60.38^\circ$ ; it undergoes hydrolysis by emulsion, forming quinol, and is probably identical with arbutin.

W. O. W.

The Preparation of Adenine from Beet Sugar Residues. KARL ANDRIK (*Zeitsch. Zuckerind. Böhm.*, 1910, 34, 567—569).—To 1 part of the residues is added 2 of water and 0.1 of copper sulphate, after an hour's boiling, 0.03 of sodium hydroxide, and then the whole is boiled for half an hour. The precipitate, separated by filtration through linen, is decomposed by hydrogen sulphide in presence of barium hydroxide (0.2—0.3 part for every 1 part of precipitate). After filtering, the clear liquid is saturated with carbon dioxide and evaporated to a syrup, when adenine separates out. Whether adenine exists as such in the residues or is a degradation product of nuclein is not ascertained, but 0.05% of pure adenine can be obtained from the residues.

E. J. R.

The Presence of Allantoin in the Seeds of *Datura Metel*. G. DE PLATO (*Chem. Zentr.*, 1910, i, 1622; from *Staz. sper. agrar. ital.*, 1910, 43, 79—85).—The seeds of *Datura Metel*, which are very

similar to those of *Nicotiana tabacum*, contain neither alkaloids nor cyanogenetic glucosides; they do, however, contain allantoin.

E. J. R.

**Betaines which Occur in Plant Tissues.** ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, 67, 46—58).—Betaine, trigocelline, and stachydrine are the three betaines which have been isolated from plant tissues. They resemble one another in general chemical properties. The suggestion is made that they are much more widely distributed than is generally thought. They are regarded as waste products (Abfallstoffe) of vegetable metabolism.

Details for the isolation of these betaines and for their separation from other bases are given (compare Abstr., 1909, ii, 605). Care is required in the separation of stachydrine and choline, as stachydrine hydrochloride is appreciably soluble in cold absolute alcohol (1 in 12 or 13). When only small amounts of stachydrine are present, the separation is most readily effected by means of potassium tri-iodide in alkaline solution. Under these conditions, the choline is precipitated, but not the stachydrine.

The method of separating choline chloride from free stachydrine by means of mercuric chloride does not always give good results.

The aurichlorides are the best compounds to use for identifying stachydrine and trigocelline and the pierate for betaine.

J. J. S.

**Production of Nicotine in Tobacco Culture.** THÉOPHILE SCHLOESING, jun. (*Compt. rend.*, 1910, 151, 23—26).—The results of experiments on a large scale are given in tabular form, the object of the inquiry being to ascertain the influence of cultural conditions on the yield of nicotine. Close planting tends to diminish the yield, whilst the proportion of sodium nitrate used as manure has little influence. Diminution of the number of leaves on the plant slightly increases the yield when this is expressed as a percentage of the dried material.

W. O. W.

**Stachydrine and Other Bases Present in Stachys Tubers and in Citrus Leaves.** ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, 67, 59—96. Compare von Planta and Schulze, Abstr., 1893, i, 447, 679; Jahns, 1896, i, 712).—Full details are given for the isolation of stachydrine from the tubers of *Stachys tuberosa* and the leaves of *Citrus aurantium*. In the former case the yield of base is 0.18% of the dry substance, and small amounts of arginine, choline, trigonelline, and alloxuric bases are also present; together with glutamine and tyrosine. The yield from the *Citrus* leaves is much the same, and choline and alloxuric bases are also present.

The hydrochloride has m. p. 235° (decomp.), and one part dissolves in 12.58 parts of alcohol at 18°. The aurichloride has m. p. 225° when rapidly heated. The platinichloride forms a yellow, anhydrous precipitate from alcohol, or orange-red crystals containing 2H<sub>2</sub>O from water. A third form, containing 4H<sub>2</sub>O and crystallising in small aggregates, is

sometimes obtained. The mercurichloride is sparingly soluble. The potassium oxalate,  $C_{17}H_{15}O_8N_2H_2CO_3$ , crystallises in needles, m. p. 109—107°, and the sulphate,  $2C_{17}H_{15}O_8N_2H_2SO_4 \cdot 2H_2O$ , is readily soluble in water. The methyl ester (Jahns, *loc. cit.*) is stable in acid solutions only. The ethyl ester is readily hydrolysed by potassium carbonate.

The precipitation of stachydrine by the addition of phosphotungstic acid to an aqueous solution of the hydrochloride of the base is not quantitative, and as much as 5% may remain in the filtrate. Similarly, the precipitation by means of mercuric chloride in either aqueous or alcoholic solution is not quantitative. Stachydrine can be identified by means of its characteristic anrichloride, and by the fact that the vapours given off when the base is heated in a glass-tube give a red coloration to a pine shaving moistened with hydrochloric acid.

The base is recovered unaltered in the urine after administration to the human system.

The constitution of stachydrine as the methylbetaine of hygric acid (Abstr., 1909, i, 324),  $CH_2 \begin{matrix} CH_2 \cdot CH \cdot CO \\ CH_2 \cdot NMe_2 \end{matrix} O$ , has been confirmed by the conversion of the base into hygric acid, and also by its synthesis from this acid (this vol., i, 62). J. J. S.

**Fixing and Staining Tannin in Plant Tissues.** ALBERT E. VINSON (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, 11).—The tannin in vegetable cells, for instance, of dates and pecan-nuts, is deposited and stained yellow by the vapour of ethyl or amyl nitrite. The specimen can be stained before being cut. For laboratory purposes a 20% solution of commercial ethyl nitrite in alcohol is recommended. J. J. S.

**Chemical and Mycological Studies on a Corn Rot having Possible Relation to the Etiology of Pellagra.** HOWARD S. REED (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, 1).—Maize when infected with pure cultures of *Diplodia zeae* and given to mice produced death in a few days. Chemical examination of the meal showed the presence of a substance soluble in alcohol, and resembling Lombroso's pellagrozein. Other crystalline substances have been isolated and their physiological properties examined. J. J. S.

**The Nitrogen-free Extract of Soola Clover (*Hedysarum coronarium*).** FRANCESCO SCURTI (*Chem. Zentr.*, 1910, i, 1632; from *Staz. sper. agrar. ital.*, 1910, 43, 5—32).—The dry matter of Soola clover contains 46.38% of nitrogen-free extract, and this was more closely examined to determine its value. It is composed mainly of three groups: (1) true sugars, partly monosaccharides with 5 or 6 C atoms and partly disaccharides; (2) sugar anhydrides formed by condensation of the monosaccharides other than dextrose, which does not appear to come into this group; (3) acids, especially such as are formed from carboxhydrates. The 46.38 parts of nitrogen-free extract are made up of 22.2 parts of dextrose, levulose, and arabinose; 2.93 of sucrose; 3.75 of galactan, araban, etc., soluble in 0.06% of sodium hydroxide;

0.67 of free organic acids; 8.43 of other compounds acidic in nature; 23.2 of gum arabic, araban, etc., insoluble in alkalis, but hydrolysed by dilute sulphuric acid (determined by difference). E. J. R.

**The Phosphorus of the Flat Turnip.** BERT L. HAETWELL and WILHELM B. QUANTZ (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxviii).—It appears that four-fifths of the phosphorus of flat turnips is present as soluble compounds, and exists mainly as inorganic phosphorus derivatives. The addition of 0.2% of hydrochloric acid to turnip juice renders it possible, after filtration, to precipitate practically all the phosphorus by the molybdic method. J. J. S.

**Rate of Extraction of Plant Food Constituents from the Phosphates of Calcium and from Loam Soil.** JAMES M. BELL (*J. Amer. Chem. Soc.*, 1910, 32, 879—884).—In a recent paper (*Landw. Jahr.*, 1910, 39, 299) on the rate of solution of two calcium phosphates and the rate of extraction of lime from a loam soil, by water saturated with carbon dioxide, Mitscherlich, Kunze, Celichowski, and Merres have come to the conclusion that the usual equation:  $dy/dt = k(A - y)$  expressing the rate of solution does not accord with their data. These authors have, however, mistaken the significance of  $A$ , which represents the concentration of the solution when final equilibrium is reached. They have taken the value of  $A$  as the total quantity of the salt which was originally mixed with the carbonated water. The present author shows that the above equation gives good results when  $A$  is given its proper significance, although the phenomenon observed is not one of solution only, but also of hydrolysis. T. S. P.

**Humic Acids of Grey Sand and Brown Sandstone.** RICHARD HORNBERGER (*Landw. Versuchs-Stat.*, 1910, 73, 221—233. Compare A. Mayer, *Abstr.*, 1905, ii, 55).—Humic acid extracted from grey sand with sodium hydroxide contained from 62.4—64.6% of carbon. Extracts obtained with ammonia yielded humic acids containing 58.6—59.9% of carbon. Brown sandstone was found to contain humic acids with varying percentages of carbon, the higher percentages agreeing approximately with the lower percentages in humic acid from grey sand.

Whilst Mayer found that ferric chloride considerably reduced the percentage of carbon in humic acid from grey sand (from 59—40%), the results of numerous experiments failed to show any diminution.

As regards the production of brown sandstone, the results seem to indicate that ferric oxide is reduced by the humic acids of the grey sand and dissolved as ferrous humate (not oxyhumate), and that lower down it is oxidised to ferric humate, in which process there is not only a change from ferrous to ferric salt, but an oxidation of the acid as well, resulting in a lower percentage of carbon. It is assumed that the oxidation is accomplished in part by bacteria. N. H. J. M.

**Chemical Colour Reactions.** C. REICHARD (*Pharm. Zentr.-h.*, 1910, 51, 607—613).—A study of the nature of colour reactions. The author summarises the results as follows: The value of a colour reaction depends: (1) on the largest possible depth of colour in combination with purity of colour; (2) the highest sensitiveness; (3) a high degree of permanency. All these conditions become of the highest value in those cases where the reaction is associated with a quantitative formation of crystalline products. L. NR K.

**Quantitative Application of the Theory of Indicators to Volumetric Analysis.** ARTHUR A. NOYES (*J. Amer. Chem. Soc.*, 1910, 32, 815—861. Compare Abstr., 1904, ii, 512; 1907, ii, 389).—A lengthy paper in which a quantitative development of the theory of indicators in a systematic form immediately applicable to the problems of volumetric analysis is given.

The equilibrium relations of the two differently coloured structural forms in which all indicators probably exist, and the equilibrium conditions under which such a pair of tautomeric substances can show sharply differentiated colours in acid and alkaline solution are first discussed. It is shown that, provided these conditions are fulfilled, the indicator can be treated in titrations as if it were a single acid or base having an ionisation constant which, although really a function of three equilibrium constants, can be directly determined either from the colour changes exhibited by it in solutions of various hydron concentration, or by any of the other methods commonly applied, for example, by measurement of the conductivity of the indicator acid or base, or by a study of the hydrolysis of its salt.

The equilibrium relations of indicators with reference to the end-point of titrations are then formulated, the end point (determined so as to correspond with a definite colour change) being reached when the hydron concentration in the titrated solution attains a definite value. A number of lecture experiments illustrating the relation between the colour change of indicators and the hydron concentration are then described, and the theory is then extended to deal with the following cases: (1) Titration of monobasic acids and monacid bases; limits beyond which the titration is impracticable. (2) Titration of two monobasic acids or of two monoacidic bases in the presence of each other. (3) Titration of dibasic acids with monacidic bases. (4) Titration of diacidic bases with monobasic acids.

In an appendix is given a summary of the values of the ionisation constants of various indicators and of various inorganic acids and bases. T. S. P.

**Luteol [as an Indicator].** L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, 67, 115).—The use of luteol was first recommended by Späth as an indicator in the neutralisation of sulphuric acid containing ammonia. The end-point is the appearance of a yellow colour. Späth's statements on the advantages of luteol are confirmed. W. D. H.

**Methylene-blue as indicator in Iodometric Titrations.** FRANK S. SINNATT (*Analyst*, 1910, 35, 309—310).—When titrating with standard iodine, the usual indicator starch may be replaced by methylene-blue. A solution is made by dissolving 0.05 gram of the dye in a litre of water, and 1 c.c. of this is then added to 50 c.c. of the solution to be titrated. The end-point is noticed by the change from blue to yellowish-green. L. DE K.

**Starch Indicator for Iodometric Titrations.** L. MATHIEU (*Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 1166—1168).—A starch solution, which is free from undissolved starch grains and gives a clear blue coloration with small amounts of iodine, is prepared from soluble starch obtained by placing starch in contact with 0.1% hydrochloric acid for some length of time, then washing the mass, drying it at a temperature of 30°, and heating the dry powder for some hours at 100°. W. P. S.

**Burette without Stopcock or Rubber Connexion.** W. ALEXANDRON (*Zeitsch. anal. Chem.*, 1910, 49, 436—437).—The apparatus consists of a calibrated tube drawn out to a fine point. To the upper part is sealed a bent tube about 5 mm. in width, and over this is pushed a long rubber tube furnished with a piece of tube drawn out to an opening 0.5 mm. diameter, and also with a pinchcock or screw clip p.

The burette is filled by suction and by means of the pinchcock; the flow from the burette is regulated. L. DE K.

**A New Form of Extraction Apparatus.** CHARLES WILSON GREENE (*J. Biol. Chem.*, 1910, 7, 503—507).—A modification of Soxhlet's extraction apparatus is described and figured. W. D. H.

**Two Cheap Appliances for Quantitative Work.** [Supports for Crucibles.] KURT ARNDT (*Chem. Zeit.*, 1910, 34, 649).—Old lids of porcelain crucibles, placed on wire gauze with a central hole, form convenient supports for platinum crucibles in the estimation of silica. Such lids, supported by fixing the handle in a slot in a match-box, form convenient surfaces on which to rest hot platinum crucible lids. C. H. D.

[Laboratory Appliances for] Analytical Practice. CARL BEGE (*Zeitsch. anal. Chem.*, 1910, 49, 427—436).—(1) When estimating the nitrogen in milks by the Kjeldahl process, it is recommended to wrap up the neck and part of the body of the digestion flask with lead foil. (2) For getting rid of the fumes when testing a number of samples, a system of lead tubes leading to a chimney has been found to act very satisfactorily. (3) Silver sand, so useful in the analysis of milk and excrement, should be tested for calcium carbonate, as this renders it unfit for use. (4) A kind of oil-cloth, black one side and green the other, is recommended instead of the usual black glazed paper in quantitative analyses. (5) An improved Kipp apparatus. The acid from the lower vessel, unless drawn off,



sometimes rises into the top one, and from there is ejected. By placing in the funnel tube of the top vessel a siphon, the other end of which is placed in a suitable vessel, the acid is removed automatically. (6) Application of Ostwald's thermo-regulator in artificial digestion. This thermo-regulator has been found very useful in digestion experiments with pepsin-hydrochloric acid at 38—40° (Stutzer's method), and may be recommended.

L. DE K.

Microchemical Studies. IV. Refractive Indices of Crystalline Chemically Individual Substances by the Immersion Method as an Aid in Practical Analysis. A. HOLLAND (*Monatsh.*, 1910, 31, 387—419. Compare Abstr., 1908, p. 1080).—Tables are given of the refractive indices, determined by the immersion method, of a very large number of inorganic and of organic crystalline substances.

The inorganic substances are derivatives of nearly all the elements in the periodic table, whilst the organic compounds comprise hydrocarbons, iodine derivatives, alcohols, acids, aldehydes, ketones, and amides of the aliphatic series, and hydrocarbons, nitro-compounds, amines, phenols, alcohols, acids, aldehydes, and ketones of the aromatic series, and terpenes, glucosides, dyes, alkaloids, and various heterocyclic bases.

C. S.

Estimation of Bromine in Monobromocamphor. ANDRÉ and LEBLIER (*J. Pharm. Chim.*, 1910, [vii], 2, 64—66).—The process is based on a reaction first noticed by Schiff, that monobromo-camphor dissolved in toluene yields sodium bromide on addition of metallic sodium.

0.5 Gram of the sample is placed in a 125 c.c. flask, 10 c.c. of toluene and 1 gram of metallic sodium are added, and the mixture is boiled for an hour, the flask being attached to an upright condenser. When cold, 30 c.c. of water are added to dissolve the excess of sodium, and, after acidifying strongly with nitric acid, 25 c.c. of  $N/10$ -silver nitrate are added, which precipitates the bromine as silver bromide. The excess of silver is then titrated by Volhard's method. The toluene does not cause any inconvenience.

L. DE K.

Method for the Estimation of Sodium Iodide in Animal Tissues. PAUL J. HANZLIK (*J. Biol. Chem.*, 1910, 7, 459—464).—The tissue is finely divided, mixed with 3—5 c.c. of 40% sodium hydroxide solution, dried at 100°, and then charred over a small flame. The residue is then oxidised by fusion with a mixture of equal parts of sodium nitrate and carbonate, which is added gradually. The mixture must not become red hot, as iodine is then lost. The white residue is extracted with water, the filtrate made up to a known volume, and an aliquot part (50 c.c.) taken for titration.

The 50 c.c. are agitated in a separating funnel with 10—15 c.c. of concentrated sulphuric acid; a small amount of sodium nitrite is added to complete the liberation of the iodine, which is extracted by shaking the liquid several times with chloroform (10 c.c.). The chloroform solution is shaken with water until free from acid, and is

then titrated with *N/10*-sodium thiosulphate solution. In control experiments, 97.8% of the iodide added was found by titration.

J. J. S.

**Evaluation of Ammonium Hydrogen Fluoride.** ERNST DEUSSEN (*Zeitsch. angew. Chem.*, 1910, 23, 1257—1258).—Commercial acid ammonium fluoride is often composed of the normal salt, and should, therefore, be tested. The pure acid salt, however, loses some hydrogen fluoride on keeping.

0.05—0.08 Gram of the sample is placed in a 20 c.c. platinum dish, a few drops of water are added, and then about 9 c.c. of standard barium hydroxide. After remaining overnight, the dish being covered with a watch-glass and placed under a bell-jar, it is placed on the water-bath and heated for four to five hours. The liquid is then transferred to a beaker, the dish is slightly rinsed, and the solution is boiled until every trace of ammonia is expelled. The dish is now rinsed with a definite amount of *N*-hydrochloric acid and then with water, the liquids being added to the contents of the beaker. After heating for some time, adding more acid if required, the excess of acid is titrated with standard barium hydroxide, with phenolphthalein as indicator. The result equals total fluorine. L. DE K.

**Estimation of Dissolved Oxygen in Waters.** WILLEM P. JORISSEN (*Zeitsch. anal. Chem.*, 1910, 49, 424—427).—Romyn (Abstr., 1896, ii, 573) devised a process which was briefly as follows. To the water collected in a special pipette is added sodium potassium tartrate, a solution of manganous chloride, and potassium iodide. Aqueous sodium hydroxide is added, and, after some time, the solution is acidified, and the iodine liberated, representing the oxygen, is titrated.

The author states that, although this process gives trustworthy results with soft drinking waters, it fails with sea-water or other brackish waters, the results being far below the actual amount present.

L. DE K.

**New Apparatus for the Estimation of Sulphur and Arsenic.** A. KLEINE (*Chem. Zeit.*, 1910, 34, 636—637).—Several modifications of the apparatus are described. For the estimation of sulphur in mild steel, dilute hydrochloric acid is used, and the gases evolved pass through a condenser with an internal glass spiral. For cast-iron and steels high in carbon, concentrated hydrochloric acid is used, and the gases pass through a spiral washing vessel placed inside the condenser. A simplified form is described for technical use.

A distillation flask which dispenses with the usual ground-in funnel is described for the estimation of arsenic. The flask and funnel are blown in one piece, the funnel being closed by a rod.

C. H. D.

**Estimation of Combustible Sulphur in Graphite.** J. CIBULKA (*Chem. Zeit.*, 1910, 34, 757).—0.5 Gram of the sample is weighed in a platinum boat, which is then placed in a combustion tube and

heated to redness in a slow current of dry oxygen. The products of the combustion are absorbed in a 10-hub apparatus containing 20 c.c. of water and 20 c.c. of 3% hydrogen peroxide. The sulphuric acid formed is afterwards titrated with  $N/10$ -sodium hydroxide, using methyl-orange as indicator. Any acidity present in the hydrogen peroxide must be allowed for.

L. DE K.

**Detection of Small Quantities of Sulphur in Inorganic and Organic Compounds.** ERNST DEUSSEN (*Zeitsch. angew. Chem.*, 1910, 23, 1258—1260).—The substance, for instance, a couple of barley grains, is powdered and mixed with 0.1 gram of sodium carbonate and the small cuttings or scrapings of a filter 9 cm. in diameter. A few c.c. of water are added, and the mass evaporated over a spirit flame. When dry, the residue is well rubbed by means of a pestle with another 0.2 gram of sodium carbonate. The mass is now introduced into a 5 cm. long filter paper cartridge, which is then wound round three or four times with a platinum wire attached to a glass rod. The cartridge is then heated for six to ten minutes in the inner flame of the blowpipe, the source of heat being Kahlbaum's "molecular" benzene, which is absolutely free from sulphur. The fused mass is then dissolved in water and the filtrate tested for sulphide by means of alkaline lead acetate (10 drops  $N$ -lead solution, 70 c.c. water, 20 c.c.  $N$ -sodium hydroxide); 0.01 mg. of  $SO_2$  may be detected by the process; it is obvious that a blank experiment should be made to ascertain the purity of the materials used. If fluorides are also present, the process is as follows. The soda-mixture (about 0.2 gram) is treated with a few drops of water and absorbed in filter paper, which is then dried on the water bath. The paper is then cut up and placed in a 2—3 cm. long paper cartridge, which is then wound round with platinum wire attached to a glass rod. After first charring the cartridge over a spirit-lamp, the cinder is heated in the inner flame of the blow-pipe burner for about ten minutes, when the usual lead test is applied.

The author criticises Ehrenfeld's and Indra's process for the detection of sulphuric acid in presence of fluorides (*Abstr.*, 1902, ii, 438) adversely, as zinc dust always contains sulphur, and, therefore, cannot be used for reduction purposes. Kahlbaum's zinc powder, however, is free from sulphur.

L. DE K.

**Volumetric Estimation of Combined Sulphuric Acid by the Barium Chromate Method.** HEINRICH ROEMER (*Zeitsch. anal. Chem.*, 1910, 49, 490—492).—A slight modification of the barium chromate process suitable for the estimation of sulphates in commercially pure samples of potassium chloride. Fifty grams of the salt are dissolved in 150 c.c. of hot water, and 4 c.c. of hydrochloric acid and 10 c.c. (or more) of  $N/2$ -barium chloride are added. When cold, a corresponding amount of potassium dichromate solution is added, and a sufficiency of ammonia to precipitate the barium chromate. The chromate remaining in the liquid, which represents the sulphate, is then titrated either by the ferrous sulphate process or the iodometric method.

The process can, of course, be used in the analysis of waters, etc. For large quantities of sulphates, Wildenstein's chromate process (*ibid.*, 1863, i, 323) is recommended.

L. DE K.

**Kjeldahl Estimations of Nitrogen.** EDWARD F. HARRISON and PERCY A. W. SELF (*Pharm. J.*, 1910, [iv], 31, 4).—In order to avoid fixed alkali being carried over into the ammoniacal distillate, the authors operate as follows:

The acid liquid (25 c.c. of sulphuric acid are used for the Kjeldahl digestion) is diluted and transferred to a long-necked, 1-litre balloon flask containing two or three pieces of granulated zinc; this is closed with a rubber cork carrying a tapped funnel and a drip-head of about 80 c.c. capacity, the latter being connected to a block-tin tube passing through a Liebig's condenser, and the other end of which dips into a measured quantity of standard acid. A sufficiency of aqueous sodium hydroxide and then more water are introduced into the flask until the total volume is about 700 c.c., and when distillation commences the distance from the top of the liquid to the bottom of the drip-head should be eight inches, and from the bottom of the drip-head to the bend where it enters the condenser also eight inches. The distillation is now carried on vigorously for forty-five minutes; on beating further, more and more alkali is carried over.

It is as well to make a blank experiment and to apply the slight correction indicated.

L. DE K.

**Estimation of Total Nitrogen by means of Formaldehyde Titration.** L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, 87, 1—7).—The following method is recommended for estimating the total nitrogen in urine. Phosphates are first removed by precipitating as ferric phosphate in the presence of acetic acid, the excess of iron is removed as basic ferric acetate, and a portion of the filtrate is heated with sulphuric acid, potassium sulphate, and copper sulphate in a Kjeldahl flask. The copper is subsequently removed as sulphide by the addition of sodium sulphide, and the excess of hydrogen sulphide boiled off. The filtrate is then neutralised with sodium hydroxide, using three drops of phenolphthalein as indicator, and the ammonium salts then estimated by Sørensen's "formaldehyde titration" method (*Abstr.*, 1908, i, 115; ii, 234).

Good results cannot be obtained by rendering the acid solution neutral to litmus before adding the formaldehyde solution.

J. J. S.

**Method for Estimating Amino-nitrogen, and its Applications.** DONALD D. VAN SLYKE (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxiv—xxxvi).—An amine or amino-acid reacts with nitrous acid, liberating free nitrogen; in the method described, this nitrogen is liberated in an atmosphere of pure nitric oxide, which is afterwards absorbed by alkaline permanganate and the pure nitrogen then measured in a gas-burette. Good results have been obtained with alanine, valine, leucine, glycine, aspartic acid, glutamic acid, phenylalanine, serine, oxyproline, tyrosine, arginine, histidine, tryptophan, leucylleucine, leucylglycine, cytosine, guanine,

and lysine (2 mols. N). Proline and glycine anhydride, which contain imino-nitrogen, do not react. Guanidine and creatine do not react, nor does the amide-nitrogen of asparagine.

The method can be used for identifying amino-acids, for determining the degree of completeness of hydrolysis of proteins, and for accurate determination of the proline obtained by the ester method. In the mixture of esters boiling below  $100^{\circ}$ , the total N is determined, and also the amino-N; the difference gives the nitrogen present as proline. Histidine and arginine can be identified without isolation, and the amino-nitrogen present in urine can be determined after destruction of the ammonia and urea.

J. J. S.

**Estimation of Nitrates.** CLARENS (*J. Pharm. Chim.*, 1910, [vii], 1, 589—593).—The process depends on the reduction of nitric acid by mercury or copper powder in the cold and the measurement of the nitric oxide produced.

The ureometer already described (Abstr., 1909, ii, 826) is used for the estimation. The pipette of the instrument is first filled with the solution to be investigated. In the reaction flask is placed sulphuric acid diluted with half its volume of water and copper powder in excess. The flask is then closed and placed in a water-bath kept at atmospheric pressure. The air in the flask is replaced by hydrogen by connecting the third tube to the stopper to a hydrogen apparatus, and finally the third tube is connected to the pipette containing the nitrate solution, the pressure in the flask being at the same time made equal to that of the atmosphere by adjusting the manometer. The nitrate solution is now run into the flask, the latter being slightly shaken to facilitate the reaction, which is over in a few seconds. The volume of gas produced is determined by the change in pressure in the manometer. The apparatus is first calibrated by making a determination with a nitrate solution of known strength.

For an apparatus of 130 c.c. capacity and a pipette holding 4 c.c., it is convenient to use nitrate solutions containing 2 to 4% of nitrates.

T. A. H.

**Pozzi-Escot's and Devarda's Methods for the Estimation of Nitrates.** EDWARD CAHEN (*Analyst*, 1910, 35, 307—308).—Pozzi-Escot's method for the reduction of nitric nitrogen to ammonia (use of aluminium-mercury couple: this vol., ii, 155) is untrustworthy, but, with a slight modification, Devarda's aluminium process gives good results.

The solution of the nitrate is treated in a Jena distilling flask with 2 to 3 grams of an alloy composed of 45 parts of aluminium, 5 parts of zinc, and 50 parts of copper. Fifty c.c. of strong aqueous sodium hydroxide are added, and the flask is at once connected to the Kjeldahl distilling apparatus. After thirty minutes, when the reduction is complete, the contents are heated to boiling, and the ammonia is distilled in a current of steam and absorbed in standard acid as usual. Methylred is recommended as a suitable indicator.

L. DE K.

**Estimation of Phosphoric Acid by means of Standard Silver Nitrate.** JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1910, 29, 794—796).—A slight modification of Holleman's silver process. The

phosphoric acid solution is rendered slightly alkaline with sodium hydroxide, using phenolphthalein as indicator, and the pink colour is then discharged with dilute nitric acid. A sufficient amount of  $N/10$ -silver nitrate is added, and then 10 c.c. of  $N/10$ -sodium acetate, and the pink colour is restored by cautiously adding  $N/10$ -sodium hydroxide; the final adjustment is then made with  $N/10$ -sulphuric acid. After diluting the whole to 150 c.c. and thoroughly shaking, the silver phosphate is removed by filtration, and in 100 c.c. of the filtrate the excess of silver is estimated by Volhard's thiocyanate process.

The process works well for calcium phosphates, but not with phosphates containing iron or aluminium.

L. DE K.

**Analysis of Commercial Phosphates.** JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1910, 29, 796—799).—5.206 Grams of the phosphate are dissolved in nitric acid and diluted to 500 c.c. Ten c.c. (0.1241 gram) are transferred to a dish and evaporated nearly to dryness on the water-bath with addition of 5 c.c. of  $N$ -sulphuric acid. When the nitric acid has been expelled, a little water is added, and the whole again evaporated; the contents are transferred to a Jena flask by means of water, and 24 c.c. of  $N/10$ -silver nitrate are added. The liquid is then titrated with  $N/10$ -barium hydroxide, using phenolphthalein as indicator. After adding 30 c.c. of  $N/5$ -sodium acetate, 10 c.c. of the solution are transferred to a 150 c.c. flask, and a little water, also a few drops of phenolphthalein, are added. Sodium hydroxide solution is added until a permanent precipitate is formed, which is then redissolved by addition of a few drops of dilute nitric acid; on adding 25 c.c. of  $N/10$ -silver nitrate, the liquid should remain clear. Ten c.c. of  $N/10$ -sodium acetate are now added, and then  $N/10$ -sodium hydroxide until a permanent pink colour is just developed; 2 c.c. of  $N/10$ -sulphuric acid are added, and the whole is diluted to 150 c.c. After thorough mixing and filtering, the excess of silver is estimated in 100 c.c. of the filtrate by Volhard's method.

If  $b$  c.c. of  $N/10$ -barium hydroxide have been used in the first titration (allowing for the sulphuric acid added), and  $S$  c.c. of silver nitrate in the second, then:

$$\% \text{CaO} = (S - b) 0.002805 \times 100 / 0.12412 = (S - b) 2.26.$$

$$\% \text{P}_2\text{O}_5 = S \times 0.002367 \times 100 / 0.12412 = S \times 1.907.$$

\* If  $b$  is less than  $S/3$ , the only constituents are the di- and tri-phosphates, and these may be expressed as:

$$\% \text{CaHPO}_3 = b \times 0.1361 \times 100 / 0.12412 = b \times 10.966.$$

$$\% \text{Ca}_3\text{P}_2\text{O}_8 = (S - 3b) 0.00517 \times 100 / 0.12412 = (S - 3b) 100/24.$$

In this process any chlorides must either be expelled or otherwise allowed for, and such substances as bone-meal should be ignited previously to solution.

L. DE K.

**New Calcium Chloride U-Tube.** RICHARD MÜLLER (*Chem. Zeit.*, 1910, 34, 649).—In order to lessen the liability to breakage, the two arms of the U-tube are bent so as to be in contact at the stoppered ends.

C. H. D.

**Decomposition of Carbonates by Heating with Sodium Metaphosphate.** WILHELM BÖTTGER (*Zeitsch. anal. Chem.*, 1910, 49, 487—489).—Sodium metaphosphate, prepared by fusing sodium

dihydrogen phosphate at a faint red heat until the weight is constant, is recommended instead of borax glass in the analysis of carbonates (estimation of carbon dioxide). Porcelain crucibles are not suitable for this process.

L. DE K.

**Electroanalysis.** FREDERIC S. KIPPING, FREDERICK M. PERRIN, GEORGE T. BEILEY, THOMAS M. LOWRY, WILLIAM J. POPE, and HENRY J. S. SAND (*Brit. Assoc. Report*, 1909, 144—145).—This report deals with the estimation of mercury by electro-deposition on gold, silver, platinum, and mercury cathodes. It is found that satisfactory results are only obtained when a mercury cathode is employed; with the other metals the results are almost invariably too high.

E. H.

**Analysis of Copper-Manganese Alloys.** Direct Titration of Iron and Manganese Present in the Same Solution. E. AZZARELLO (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 552—555).—The following method has proved to be rapid and accurate for the analysis of alloys containing about 95% copper, 4.5% manganese, and smaller quantities of iron and lead. The alloy is dissolved in nitric acid, and the latter is then driven off by heating with sulphuric acid, and in the acid solution, previously warmed to 60°, the copper is estimated by electrolysis with a current of 0.3—0.27 ampere per sq. dcm. at 1.7—2.5 volts. The solution is treated with small quantities of 3% hydrogen peroxide to dissolve any precipitate of oxides of iron and manganese, and to destroy any permanganic acid which may have been formed. The excess of hydrogen peroxide is removed by the addition of the requisite quantity of *N*/100-permanganate, and the liquid is reduced with zinc and titrated with permanganate. When the iron has been estimated in this way, the greater part of the acid is neutralised with sodium hydroxide, a slight excess of zinc oxide is added, and the manganese in the solution is then titrated with *N*/10-permanganate, allowance being made in the calculation for the manganese which has been added in the previous titrations.

R. V. S.

**Volumetric Estimation of Manganese.** Z. KARAOGLANOFF (*Zeitsch. anal. Chem.*, 1910, 49, 419—424).—A modification of Völhard's method (hot titration of manganous sulphate with permanganate in presence of zinc sulphate) which does not work well in presence of iron, and has also other drawbacks. If, however, instead of the sulphate, the nitrate is taken, and about twice or thrice the weight of ferric nitrate is added, the titration gives good results. Instead of ferric nitrate, silver nitrate may be used with advantage for rapid work.

Very unfavourable results are obtained by using free nitric acid or zinc, aluminium, or barium nitrates, or by simply titrating the manganous nitrate without an additional salt.

L. DE K.

**Rapid Method for the Detection and Colorimetric Estimation of Small Quantities of Vanadium in Steel.** PAUL SLAWIE (*Chem. Zeit.*, 1910, 34, 648).—For the detection of vanadium in steel,

0.25 gram of turnings is dissolved in 4 c.c. of nitric acid, D 1.20, and warmed; 0.3 gram of solid ammonium persulphate is then added, and, after heating until the evolution of gas ceases, the tube is cooled. On the addition of 3 to 4 c.c. of phosphoric acid, D 1.30, the yellow colour of the iron disappears, and the solution is pale pink. After stirring, 3 to 4 c.c. of hydrogen peroxide are run in down the side of the tube from a pipette. A reddish-brown ring is formed, even by 0.01% of vanadium. The method becomes a quantitative one for steels containing less than 0.5% of vanadium, a steel of known content of vanadium being used as a colorimetric standard, or a steel free from vanadium, together with a dilute titrated solution of vanadium, may be employed.

For the exact estimation of vanadium in steel, 20 grams of turnings are dissolved in 60 c.c. of sulphuric acid, D 1.20, and 200 c.c. of water, and the solution nearly neutralised while hot with zinc oxide, the neutralisation being completed by adding zinc oxide, freshly precipitated with ammonia, until a slight turbidity remains. After boiling for fifteen minutes in a covered beaker, the precipitate, containing the vanadium and a little iron, is collected, washed with hot water, dried, and ignited. It is then fused with sodium hydroxide and potassium nitrate, dissolved, and filtered. The vanadium is best estimated in the filtrate by precipitating with manganous chloride, dissolving the precipitate in hydrochloric acid, heating with sulphuric acid, and titrating with potassium permanganate. C. H. D.

**Separation of Bismuth from Lead and the Analysis of Bismuth-Lead Alloys.** HARRY F. V. LITTLE and EDWARD CAREN. (*Analyst*, 1910, 35, 301—306).—The process recommended by Benkert and Smith (double precipitation as bismuth formate: *Abstr.*, 1897, ii, 435) is found to give good results. When applying this to commercial alloys, the authors operate as follows:

0.5—0.7 Gram of the sample is dissolved in a little nitric acid diluted with water, and any precipitate is collected, washed with hot dilute nitric acid (1:2), and then with water. It is then rinsed into a beaker with a little water, and heated for a few minutes with 25 c.c. of ammonium hydrosulphide. The solution is then filtered through the same filter, and the insoluble sulphides, after being washed, are dissolved in a little nitric acid, and the solution added to the main filtrate. This is then evaporated to a small bulk to expel most of the nitric acid, and, after neutralising as far as possible with solution of sodium carbonate, the bismuth is removed by boiling with sodium formate; to completely free the precipitate from lead, a second treatment with sodium formate is necessary. The bismuth is finally weighed as phosphate according to Stähler's method (*Abstr.*, 1907, ii, 655).

In the filtrate from the bismuth, the lead is estimated in the usual way as sulphate; the filtrate contains any cadmium which may then be precipitated as carbonate, and weighed as oxide, or it may be deposited electrolytically in presence of potassium cyanide. The tin may be deposited electrolytically from its ammonium sulphide solution, or else converted as usual into oxide.

L. DE K.



**Estimation and Separation of Palladium.** ALEXANDER GUTHRIE and FERDINAND FALCO (*Zeitsch. anal. Chem.*, 1910, 49, 492—493).—A correction of some statements in the authors' paper on this subject (this vol., ii, 459).  
L. DE K.

**Method for the Complete Extraction of Chloroform Vapour from Air and for its Estimation.** MAURICE NICLOUX (*Bull. Soc. chim.*, 1910, [iv], 7, 561—567).—The air containing chloroform vapour is drawn by means of an aspirator up a glass-tube 1 metre long and 30 mm. wide, filled with glass balls, 3—5 mm. in diameter. Alcohol is allowed to run slowly down this tube, and in this the chloroform vapour dissolves, and the solution is collected in a bottle at the base of the tube. A wash-bottle containing alcohol may be inserted before the extraction tube, so that the rate at which the air is drawn through may be estimated roughly. Finally, the alcohol in the wash-bottle is mixed with that in the receptacle, and the whole boiled with potassium hydroxide in a reflux apparatus, and the potassium chloride formed by the decomposition of the chloroform estimated by Mohr's method after exact neutralisation. Air containing chloroform may be passed through this apparatus at the rate of 80 to 100 litres per hour without loss of chloroform. The apparatus may prove useful for other quantitative gas absorption work (compare Davis, *Abstr.*, 1909, ii, 615).  
T. A. II.

**Refractive Indices of Water-Alcohol Mixtures.** D. SIDERSKY (*Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 1168—1169).—The refractive index of a mixture of alcohol and water increases in proportion to the alcohol-content, the increase being about 0.0005 per degree of the Gay Lussac scale. A maximum value is reached at a concentration of 85.69° Gay Lussac, the mixture then having  $n_D^{20}$  1.36587; the value then diminishes as the percentage of alcohol increases, absolute alcohol having  $n_D^{20}$  1.36229, a value also shown by a mixture reading 59.23° Gay Lussac. Solutions containing more than 50% of alcohol should, therefore, be diluted with a known quantity of water before the alcoholic strength is estimated by means of the refractometer (compare *Abstr.*, 1907, ii, 821).  
W. P. S.

**New Method for the Estimation of Glycérol in Wines.** CONSTANTIN BÉYS (*Compt. rend.*, 1910, 151, 80—81).—Fifty c.c. of wine (25 c.c. if the density is less than 5° Beaumé) are neutralised with barium hydroxide and concentrated, below 70°, to a syrup. Sand is added, and the glycerol extracted with 40—50 c.c. of acetone on a water-bath below 56°. The process is repeated until the filtered liquid amounts to at least 200 c.c. Two aliquot portions are evaporated without boiling, and the sugars determined in one by Fehling's solution. The other portion is dissolved in five times its weight of water, and treated with solid barium hydroxide (4/5th of the weight of the sugar). Sand is then added, and the mixture extracted four times with 25 c.c. of acetone. The extract is evaporated at 56°, dried at 60—65°, and weighed. If the wine contains less than 5% of sugar, the first extraction is unnecessary.  
W. O. W.

**Potassium Ferrocyanide as an Indicator in the Estimation of Dextrose.** ETTORE SELVATICI (*Bull. Assoc. chim. Sucr. Dist.*, 1910, 27, 1179—1184).—The following manner of employing potassium ferrocyanide as an indicator of the end-point of the titration of Fehling's solution with dextrose solutions is recommended. Ten c.c. of Fehling's solution, 10 c.c. of water, and 10 c.c. of a 1.5% potassium ferrocyanide solution are placed in a test-tube 25 cm. long and 3 cm. in diameter, boiled, and the dextrose solution is run in from a burette, the contents of the tube being maintained at a boiling temperature during the whole of the time taken for the titration. When all the cupric salt has been reduced by the added sugar, the mixture becomes quite colourless. W. P. S.

**Bang's Method of Estimating Sugar, and the Preservability of the Reagents Employed in Titration.** A. C. ANDERSEN (*Biochem. Zeitsch.*, 1910, 23, 157—164).—It was found that Bang's hydroxylamine solution can be kept without appreciable change for prolonged periods if protected from light, whereas the copper solution undergoes change when kept both in the light and in the dark, and more rapidly in the former condition than in the latter. S. B. S.

**Colorimetric Method of Estimating Small Quantities of Sugar by means of the  $\alpha$ -Naphthol Test.** ROBERT FRAILONG (*Bull. Assoc. ch. n. Sucr. Dist.*, 1910, 27, 1188—1190).—The author recommends the preparation of photographic standards for use in comparison; for this purpose, solutions containing known quantities of sugar are treated with the reagent and sulphuric acid, definite proportions of each being employed (2 c.c. of sulphuric acid, 1 c.c. of the sugar solution, and 4 drops of a 2.5%  $\alpha$ -naphthol solution). The colorations produced are then suitably illuminated and photographed on an autochromatic plate (Lumière). The coloration obtained with any sugar solution under examination is compared with these photographic standards. W. P. S.

**Estimation of the Total Soluble Fatty Acids in Fats.** ALBERT BRUNO (*Ann. Falsif.*, 1910, 3, 238—239).—The process described is a continuation of the method usually employed for the estimation of the saponification number of fats. After the final titration, the addition of the titration acid is continued until a quantity, exactly equivalent to the amount of alkali used, has been added to the solution. Hot water is then added to the mixture (which should be contained in a flask graduated at 151.8 c.c. at a temperature of 50°) until the volume of the whole measures 151.8 c.c. at 50°. After mixing, the liquid is cooled, filtered, and the soluble fatty acids are titrated in an aliquot portion of the filtrate. W. P. S.

**A New Method for Estimating Fat and Fatty Acids in Faeces.** OTTO FOLIN and A. H. WESTWORTH (*J. Biol. Chem.*, 1910, 7, 421—426).—The dried material is pulverised and extracted with a mixture of ether and hydrochloric acid for twenty hours; the residue

of the extract is extracted with light petroleum, and the residue of this extract is weighed; this gives the total weight of neutral fats and fatty acids. It is dissolved in benzene, a few drops of 0.5% alcoholic solution of phenolphthalein added, and the mixture heated to near its boiling point. It is then titrated with a standard sodium ethoxide solution until the maximum colour of the indicator is obtained; this gives the total fatty acid (both that free and that present in the form of soaps). The neutral fat is obtained by subtracting the value of the second estimation from the first. It is not regarded as possible to determine the free fatty acids and the soaps separately. Increase in the total fats of the faeces is mainly due to increase of the fatty acid, and this is mainly stearic acid. W. D. H.

**A Simple Apparatus for Bromination.** HENRIK BULL and LELF SÆTHER (*Chem. Zeit.*, 1910, 34, 649).—The apparatus is specially designed for the preparation of the bromides of unsaturated fatty acids. The brominating flask is placed in an inclined position, and is provided with a glass tubular stirrer, expanded into a spoon at the lower end and slightly bent. The stirrer is fitted with a pulley and is mechanically driven, and the bromine is allowed to fall through it from a capillary tube, so that 1 c.c. is admitted in about eight minutes. Control analyses are given to show the accuracy of the estimation of unsaturated acids by means of it. C. H. D.

**Estimation of Tartaric Acid in Wine Products.** CONSTANTIN BÉYS (*Bull. Soc. chim.*, 1910, [iv], 7, 697—699).—The process is designed to avoid the errors of Goldenberg and Géromont's method (*Abstr.*, 1898, ii, 465, 545), and depends on the decomposition of the crude tartrate with hot dilute sulphuric acid, extraction of the tartaric acid by means of a mixture of alcohol and ether, decomposition of any ethyl tartrate formed by ebullition with excess of potassium hydroxide in alcohol, and precipitation of the tartaric acid as potassium hydrogen tartrate by the addition of acetic acid. The precipitated tartrate is finally titrated with standard alkali, using phenolphthalein as indicator. Precise details and quantities of reagents to be used are given in the original. T. A. H.

**Conventional Methode for the Analysis of Materials [Tartrates] Adopted by the Seventh International Congress of Applied Chemistry.** P. CARLES (*Bull. Soc. chim.*, 1910, [iv], 7, 586—588).—From a thoroughly representative sample of known weight the grosser impurities are picked out and weighed. The residue is broken up so as to pass through a 0.5 mm. sieve and then ground. The potassium hydrogen tartrate is determined by placing 2.35 grams in 400 c.c. of water in a 500 c.c. flask, boiling for five minutes, cooling, and making up to 500 c.c. The flask is then shaken, and the contents filtered. Of the filtrate, 250 c.c. are heated to boiling in a porcelain dish and titrated, using  $N/4$  potassium hydroxide with litmus paper as indicator, a similar determination with pure potassium hydrogen tartrate being made at the same time as a control.

For the estimation of "total tartaric acid," 6 grams of material

containing over 45%, or 12 grame of poorer material are thoroughly mixed with 18 c.c. of hydrochloric acid (D 1.10) in a 200 c.c. beaker, macerated during ten to fifteen minutes, washed into a measuring flask, made up to 200 c.c., and 100 c.c. collected in a dry, conical flask, after filtration through dry paper. This is heated to boiling, and 10 c.c. of a solution of potassium carbonate (D 1.49) added gradually. The mixture is shaken, slowly heated, and finally boiled during twenty minutes. The contents are then cooled, made up to 200 c.c., filtered through dry paper, and 100 c.c. of the filtrate are evaporated to 15 c.c. in a porcelain capsule. To this, 3.5 c.c. of glacial acetic acid are added in drops, and the mixture stirred during five minutes. After ten minutes, 100 c.c. of alcohol of 95° are added with continuous agitation, and, after standing ten minutes, the precipitate is collected, washed with alcohol until the latter is no longer acid, and the filter paper and precipitate transferred to a porcelain capsule containing 200 to 300 c.c. of water, boiled, and then titrated with  $N/4$ - or  $N/5$ -potassium hydroxide solution, using litmus paper as indicator. Deduction must be made from the percentage of "total acid" found, for insoluble matter not reckoned in making up the volume of the solution; the corrections are given in brackets after the percentages to which they correspond: 20 (0.8), 30 (0.7) 40 (0.6), 50 (0.25), 60 (0.15), 80 (0.10).

T. A. H.

**Detection of Glycuronic Acid in Urine.** GUIDO GOLDSCHMIEDT (*Zeitsch. physiol. Chem.*, 1910, 67, 194).—The author's test for glycuronic acid (this vol., ii, 555) is interfered with by the presence of nitrates, which by themselves give a very similar colour. Rühmann has described nitrates in human urine, which come from the food, but they are absent from the urine of rabbits and dogs. In man, a nitrate-free diet can easily be adopted in laboratory and clinical work. In the present research no nitrates were found in the urine of man, cat, dog, or rabbit.

W. D. H.

**Estimation of Hydrocyanic Acid in the Blood and Tissues After Death.** AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xlvii—xlix; *J. Physiol.*, 40).—The method is colorimetric, and is based on the method of Hlasiwetz as recently applied by Guignard. A colour scale is prepared by mixing dilute hydrocyanic acid and picrate mixture in various concentrations, and the estimation is made by matching the colour given by the fluid under investigation, or of its distillate, with picrate mixture, with that of the colour scale.

W. D. H.

**Estimation of Benzoic Acid in Foods.** FÖEKE H. VAN DER LAAN and H. TYDENS (*Chem. Weekblad*, 1910, 7, 603—615).—Fifty to seventy c.c. of the aqueous alkaline extract are acidified with dilute sulphuric acid, a few drops of alcohol are added, and the benzoic acid is extracted by means of 60 c.c. of benzene in a suitable extraction apparatus. After five hours, the benzene is washed twice with 5 c.c. of cold water to remove other acid substances, and then titrated with  $N/10$ - or  $N/50$ -alkali, using phenolphthalein as indicator. After adding a few more

c.c. of alkali, water is added, and, after shaking, the alkaline layer is drawn off. The solution is then acidified with a few c.c. of dilute sulphuric acid, and the benzoic acid extracted by shaking with 50 c.c. of ether; the ether is decanted into a long, narrow beaker containing 5—10 c.c. of water, and allowed to evaporate, when crystals of the acid will become visible on the sides of the beaker. A few drops of the aqueous liquid are then tested for the possible presence of salicylic acid by means of a drop of 1% ferric chloride. If this is absent, the presence of benzoic acid may be confirmed by warming for ten minutes with 2 c.c. of 0.5% hydrogen peroxide, and, after cooling, testing with ferric chloride, which will then give the characteristic violet colour. If salicylic acid is present, the process is modified as follows:

The benzene solution is titrated for the joint acids, then rendered alkaline, and the aqueous layer is separated from the benzene.

After carefully neutralising with *N*/10-sulphuric acid, the solution is made up to 100 c.c., and in an aliquot part the salicylic acid is estimated colorimetrically by means of ferric chloride.

If by way of a check it is desired to estimate the benzoic acid directly, it may be isolated in a pure condition by acidifying the remainder of the liquid and shaking with ether. On evaporating the ether, the residue may be freed from salicylic acid by warming with a slight excess of alkaline permanganate, which does not affect the benzoic acid. After removing the excess of permanganate by means of sulphurous acid, the benzoic acid may be recovered from the acidified liquid by extraction with benzene, and then be again titrated. If "saccharin" is also present, the method becomes more complicated, and steam distillation must be resorted to.

L. DE K.

\* **Estimation of Salicylic Acid by Distillation of its Dilute Aqueous Solutions.** NOEL C. CASSAL (*Chem. News*, 1910, 101, 289).—The estimation of salicylic acid in such liquids as wine, etc., by extraction with a solvent is often vitiated by the simultaneous extraction of other substances; further, when an attempt is made to separate the salicylic acid by distillation, very variable results are obtained, owing to the fact that many organic substances have an inhibitory effect on the distillation of the acid. The author therefore recommends the following process, which is a combination of the extraction and distillation methods. The salicylic acid is first extracted from the wine by means of chloroform, and the chloroform solution is then shaken several times in succession with dilute alkali solution in order to obtain the salicylic acid in aqueous solution. The alkaline solution is acidified with phosphoric acid and distilled, the salicylic acid passing over into the distillate being estimated colorimetrically. When 90 per cent. of the solution is distilled, from one-fifth to one-tenth of the salicylic acid present is found in the distillate; the quantity found is therefore multiplied by the factor 5.5 to obtain the amount present originally.

W. P. S.

**Determination of Aldehydes in Distilled Liquors.** MARIANO DEL ROSARIO (*Philippine J. Sci.*, 1910, 5, 29—32).—This process is a modification of Ripper's method. Twenty-five c.c. of the aldehyde

hyde solution, which must contain about 0.5% of the aldehyde, are mixed with 50 c.c. of 4% potassium hydrogen sulphite in an Erlenmeyer flask, which is stoppered and set aside for fifteen minutes, being occasionally shaken. Meanwhile, 50 c.c. of the sulphite solution are titrated by  $N/10$ -iodine and starch paste. At the expiration of the fifteen minutes, the mixture is also titrated. The difference between the two titres is a measure of the bisulphite combined with the aldehyde. The amount of aldehyde is given by the expression  $nM/20,000$ , where  $M$  is the molecular weight of the aldehyde, and  $n$  is the number of c.c. of  $N/10$ -iodine used.

C. S.

**Detection of Hexamethylenetetramine in Musts and Wines.** BORTS (*Ann. Falsif.*, 1910, 3, 250—253).—The test described by Voisenet (this vol., ii, 466) was found to be quite trustworthy; as small traces of formaldehyde may be found in the distillate from wine which has not been treated with hexamethylenetetramine (these traces being formed when an acid, saccharine liquid, such as wine, is heated), it is doubtful whether there is any practical advantage in using a test as sensitive as the one in question; erroneous conclusions may be formed should a mere trace of formaldehyde be detected. The usual magenta-sulphurous acid reagent is sufficiently sensitive for all ordinary purposes, and the coloration it yields is characteristic of formaldehyde if the test be applied in sulphuric acid solution.

W. P. S.

**The Influence of Urea on the Estimation of Amino-acids by Formaldehyde.** L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, 67, 105—114).—The explanation given by Henriques and Sørensen why the formaldehyde method gives too low results in mixtures of ammonia and amino-acids is correct. It does not, however, appear necessary that methyleimine should be first present, for probably ammonia and ammonium compounds have the same action. Other amino-compounds are also able to effect an exchange of  $NH_2$  for  $OH$ . The addition of urea inhibits the opposing action of ammonia compounds and amino-acids. The practical outcome is that in urine, the method gives correct results.

W. D. H.

**Analysis of Ferrocyanides.** HAROLD G. COLMAN (*Analyst*, 1910, 35, 295—301).—A reply to Skirrow (this vol., ii, 361). The Feld magnesium chloride process as used by the author (*ibid.*, 1908, 33, 261) has again proved to be very satisfactory.

L. DE K.

**The Iodometric Estimation of Potassium Ferro- and Ferricyanide.** WERNER MECKLENBURG (*Zeitsch. anorg. Chem.*, 1910, 67, 322—338).—Potassium ferricyanide may be estimated by the iodometric method, according to the equation  $K_3Fe(CN)_6 + KI = K_4Fe(CN)_6 + I_2$ , in the presence of a zinc salt. The salt to be analysed (0.5—1.5 gram) is dissolved in 500—750 c.c. of water, and 10—15 c.c. of concentrated hydrochloric acid are added. The addition of 10—15 grams of potassium chloride renders the precipitate less colloidal. After adding 10—20 c.c. of a 10% solution of potassium iodide and 10 c.c. of a  $N/1$ -solution of zinc sulphate, the liquid and precipitate are allowed to

remain for three minutes in a stoppered flask, starch solution is then added, and nearly a sufficient quantity of  $N/10$ -sodium thiosulphate. After three minutes the titration is completed. The results are slightly (0.1%) too low, owing to adsorption by the precipitate. Similar results are obtained in acetic acid solution.

Potassium ferrocyanide may be estimated in the same way if previously oxidised. The solution in hydrochloric acid, as above, is oxidised with approximately  $N/10$ -permanganate solution, the excess being removed by oxalic acid. The estimation then proceeds in the usual way.

Potassium ferrocyanide may be estimated directly by the following method. The salt is dissolved in 600–800 c.c. of water and 10–15 c.c. of concentrated hydrochloric acid; a concentrated solution of 15–20 grams of sodium acetate is then added, and  $N/10$ -potassium permanganate solution is run in until the red colour persists. Ten c.c. of 10% potassium iodide solution are added, followed by starch, and, after three minutes, the iodine is titrated with  $N/10$ -sodium thiosulphate. Acetic acid usually contains reducing substances, and should not be used.

Pure potassium ferrocyanide is prepared by dissolving repeatedly in water and precipitating with alcohol.

When both ferricyanide and ferrocyanide are present, sodium acetate is added to the hydrochloric acid solution, and the ferrocyanide is estimated by the permanganate method. Hydrochloric acid, potassium iodide, and zinc sulphate are then added, and the total ferricyanide is estimated as described above.

C. H. D.

Strzyzowski's "Double Ureometer." O. VON SPINDLER (*Chem. Zentr.*, 1910, 1, 1549–1550; from *Schweiz. Woch. Chem. Pharm.*, 1910, 48, 91–93).—The author duplicates his apparatus and carries out an estimation with a known quantity of urea (2–5 c.c. of a 1% solution) simultaneously with the estimation proper. In this way the necessity is obviated for the temperature and pressure corrections and for allowance for undecomposed urea. The nitrogen is collected in graduated tubes immersed in water, both tubes being in the same water vessel.

E. J. R.

The Estimation of Ammonia and Urea in Blood. CHARLES F. L. WOLF and MCKIM MARRIOT (*Biochem. Zeitsch.*, 1910, 23, 165–170).—The ammonia and urea were estimated in the same portion of the blood. After defibrination and filtration, 50 c.c. of saturated sodium chloride solution were added to 100 c.c. of blood, and to this mixture were added, with constant stirring, 250 c.c. of methyl alcohol. The liquid was then filtered off from the precipitate through a Löben pressure filter, and the filtrate placed for some time in an ice-chest and then filtered from the small deposit which settled. In 100 c.c. of this filtrate, the ammonia was estimated by the addition of 10 c.c. of 2*N*-sodium carbonate solution, and evaporation in a vacuum, the ammonia thus set free being collected in Drechsel flasks containing  $N/50$ -sulphuric acid. The amount thus obtained could then be estimated by titration. In the residual liquid which was not

evaporated off, the urea could be estimated by either the Fölin magesium chloride method, or the Pfäfer-Schöndorf phosphoric acid method. The ammonia estimations gave satisfactory results, whereas the urea estimations were not quite so concordant. S. B. S.

**A Reagent for the Biuret Test.** WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, lx).—The reagent recommended consists of a 1% solution of potassium hydroxide, treated with sufficient 3% copper sulphate to impart a slight blue colour to the solution. All the required copper is held in solution.

W. D. H.

**Estimation of Caffeine in Kola.** DESVIGNES (*J. Pharm. Chim.*, 1910, [vii], 2, 20—22).—Fifteen grams of the dried Kola powder are mixed with 10 grams of magnesium oxide, and enough water is then slowly added to get a semi-liquid paste. The whole is left in a warm place, with occasional stirring, until the mass has become perfectly dry. It is then placed in a percolator and moistened with 30 c.c. of chloroform. After three or four hours, the chloroform is drawn off and the mass exhausted by percolating six times in succession with 20 c.c. of chloroform. The chloroform is then allowed to evaporate in a tared dish or recovered by distillation, and the caffeine is dried in the water-oven and weighed; it should be quite white. L. DE K.

**Detection of Morphine in Organs.** GUNNAR JÖRGENSEN (*Zeitsch. anal. Chem.*, 1910, 49, 484—486).—In the usual process for the detection of morphine, the acid liquid is first shaken with pure ether (or other solvent) to remove impurities, and, after rendering alkaline, the alkaloid is extracted with hot amyl alcohol, ethyl acetate, or chloroform containing alcohol.

The author, however, prefers using, instead of these solvents, ether containing 1 to 1.5% of alcohol; as morphine is but sparingly soluble therein, the extraction should be repeated ten times, but a very pure alkaloid is obtained. If highly coloured liquids have to be extracted, it is better to use amyl alcohol first; the solution is then shaken with acidified water, and from this the morphine is recovered by the ether-alcohol mixture as directed.

L. DE K.

**Estimation of Morphine in Cases of Poisoning.** CHARLES R. SANGER and WILLIS A. BOUGHTON (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xxxvii—xxxix).—Kobert's test may be made approximately quantitative. The morphine residue is treated with a few drops of a dilute solution of formaldehyde in sulphuric acid; after a time the blue residue is diluted, neutralised with sodium hydroxide, and the resulting brown solution is made up to a definite volume in a Nessler tube. Comparison standards are made by treating known amounts of morphine in the same way.

W. D. H.

**Analysis of Proteins.** THOMAS B. OSBORNE and D. BRESEE JONES (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, viii—ix).—Loss may result from incomplete hydrolysis, formation of humin,



incomplete separation of glutamic acid, and incomplete esterification. Analysis of a mixture of pure amino-acids in the same proportion as they were obtained from zein showed that a loss of from 28 to 57% may occur.

W. D. H.

**Estimation of Peptide Compounds in Proteins and in Their Cleavage Products.** VALDEMAR HENRIQUES and J. K. GJALDRIK (*Zeitsch. physiol. Chem.*, 1910, 67, 8—27).—Experiments have shown that when Witt's peptone is evaporated twice to dryness on the water-bath there is still some nitrogen present as peptide nitrogen (some 12-2% of the total originally present).

Complete hydrolysis can be brought about by boiling with 20% hydrochloric acid for twelve hours.

The same holds good for many other proteins, but in the case of egg-albumin the hydrolysis is not complete even after twelve hours' boiling with concentrated hydrochloric acid. With substances which are readily hydrolysed, or which have previously undergone prolonged hydrolysis with enzymes, six hours' boiling is sufficient to complete the hydrolysis. Complete hydrolysis can also be brought about by heating at 150° for 1.5 hours, or at 120° for three hours, in sealed tubes with 3*N*-hydrochloric acid. Sulphuric acid is not so efficient.

In all cases the total nitrogen present as amino-acids and as ammonia was estimated by Sørensen's formaldehyde titration method, the ammonia then estimated by distillation under reduced pressure with methyl alcohol and barium hydroxide, and the amino-acids by difference. The process of heating with hydrochloric acid at 150° or 180° tends to increase the amount of ammonia nitrogen beyond the value obtained by merely boiling with hydrochloric acid. Temperatures above 150° should not be used, as under such conditions the amino-acids are liable to undergo secondary decompositions.

Attention is called to the fact that Abderhalden had drawn the conclusion that proteins can be completely hydrolysed by contact with trypsin and erepsin for several months.

The authors' experiments show that this is not so, and that the products still contain peptide compounds.

J. J. S.

**The Use of Invertase in the Determination of the Alkalinity or Acidity of Biological Fluids.** C. S. HUDSON and WILLIAM SALANT (*Proc. Amer. Soc. Biol. Chem.*, 1909; *J. Biol. Chem.*, 1910, 7, xiii).—Yeast invertase loses on dialysis its acid and most of its activity; the latter returns on the addition of acid. If its activity in water is taken as 300, in various bloods this is lowered to figures varying from 266 (dog's blood) to 69 (pig's blood). If blood is dialysed, it loses the power of lowering the activity of invertase, showing that the lowering is due to salts.

W. D. H.

# General and Physical Chemistry.

**The Relative Duration of the Rays of Calcium in the Spark with Self-Induction.** GUSTAVE A. HEMSALECH (*Compt. rend.*, 1910, 151, 220—223).—By the use of a method previously described (*Compt. rend.*, 1903, 141, 1227; 1910, 150, 1743), the relative duration of the calcium rays has been measured. For the "arc" rays the time of duration is, as in the case of iron, nearly proportional to their intensity, and varies between 93 and 233 microseconds. The coefficient of augmentation produced by increasing the capacity from 0.0023 to 0.012 microfarad was nearly the same (1.4 to 1.5) for all rays except the strongest, 4227, for which it was 1.25. The duration of the "spark" rays was shorter, considering their intensity, than the "arc" rays, the most brilliant of all having shorter duration than many of the "arc" rays. For the impurities, strontium and aluminium; the duration of certain rays was also determined, and as these sometimes differ from the rays of the pure substance, useful indications may in certain cases result from the method in analysing a substance containing unknown impurities.

F. S.

**Phosphorescence.** GEORGES URDAIN (*Bull. Soc. chim.*, 1910, [iv], 7, i—xiii).—A lecture delivered before the French Chemical Society.

E. H.

**A Photographic Method of Recording  $\alpha$ -Particles.** WILLIAM DUANE (*Compt. rend.*, 1910, 151, 228—230\*).—In the method described, the image of a gold-leaf of a sensitive electroscopie is thrown by means of a Nernst lamp and lens on a slit, behind which a Kodak film is moved transversely to the slit by clockwork. The connecting wire to the electroscopie passes through an ionisation chamber containing polonium (which discharges it after each charge) to the electrode of a small ebonite box of less than 1 c.c. volume, into which  $\alpha$ -particles enter through a small hole in the bottom covered with thin mica, and which is exhausted to 1 or 2 cm. pressure. The bottom of the box is of metal connected to a high tension battery of accumulators, the potential being arranged so that a spark just does not pass. By this modification of Rutherford and Geiger's apparatus, a photographic record of the sudden movements of the gold-leaf produced by the individual  $\alpha$ -particles is obtained. Specimen portions of the film with and without a source of  $\alpha$ -particles show the effect of the latter with great clearness.

F. S.

**The  $\beta$ -Activity of Uraninite.** STEWART J. LLOYD (*J. Physical Chem.*, 1910, 14, 509—527).—The percentage  $\beta$ -activity contributed by the  $\beta$ -ray constituents of uraninite has been found to be:

Uranium-X .....	32.1	} Total 95.2%.
Radium-B .....	16.1	
Radium-C .....	36.1	
Radium-E .....	10.9	

\* and *Le Radium*, 1910, 8, 196—198.

The electroscope employed was a cylinder 40 cm. high and 40 cm. diameter. The  $\beta$ -activity of the powdered uraninite was corrected for absorption in the substance by extrapolating the curves of activity, obtained with increasing thickness of films, back to the origin, and for loss of emanation from the powdered uraninite which was measured.

The proportions due to uranium-*X* and radium-*B* and -*C* were obtained by comparing the  $\beta$ -activities of these substances obtained from known quantities of uranium and radium. Many observations on the separation of uranium-*X* from uranium and impurities are described. Stirring soot, obtained freshly from the burning of naphthalene, into acetone solution of uranyl nitrate, extracting the soot with hydrochloric acid, adding iron, and precipitating the iron and uranium-*X* with excess of ammonium carbonate, gives good results. The only way of freeing ammonium-*X* from iron is to dissolve in concentrated hydrochloric acid, and to extract with freshly distilled ether saturated with hydrogen chloride, when the uranium-*X* is left in the aqueous solution. In the electroscopes employed, 26.7% of the total ionisation due to uranium-*X* was contributed by the soft  $\beta$ -rays, and these are not included in the foregoing table. The existence of radio-uranium is questioned. Measurements of the active deposit produced by the emanation of a known quantity of radium gave the proportion of  $\beta$ -rays due to radium-*B* and -*C* together, that due to the latter alone being determined by volatilising the former at 700°. The radio-lead was chemically separated from uraninite with added lead, and left to accumulate the equilibrium amount of radium-*E*, which was then separated from the lead solution by adding a drop of iron and sodium hydroxide in excess, when the radium-*E* remains undissolved with the iron. The  $\beta$ -rays of uraninite, in the electroscope used, gave an ionisation equal to the  $\alpha$ -rays of 23.5 sq. cm. of a thick film of  $U_3O_8$ .  
F. S.

The Experimental Testing of the Question of the Nature of the  $\gamma$ -Rays. II. Egon R. von SCHWEIDLER (*Physikal. Zeitsch.*, 1910, 11, 614—619. Compare this vol., ii, 376).—In a further purely theoretical discussion of the nature of the variations in the intensity of  $\gamma$ -rays from instant to instant to be expected on the various "corpuscular" and "impulse" theories, various criticisms of the first paper, resulting from a correspondence with Sommerfeld, Planck, Bragg, and Campbell, are taken into account, and these modify the earlier conclusions. The most important refer to the possibility that, in addition to the other probability variations, the number of pairs of ions produced by the individual  $\gamma$ -ray in the gas may vary (Campbell), and to the established fact that the  $\gamma$ -ray ionisation is largely, if not wholly, due to the soft secondary radiation and not to the primary radiation directly (Bragg). The various hypotheses are reviewed in detail, and the nature of the variations theoretically to be expected in each case worked out. The conclusion is drawn that an experimental means of testing the two theories is not possible if the  $\gamma$ -ray ionisation is produced by secondary rays, although the absolute magnitude of the variations of ionisation is within the limit of experimental detection if whichever theory is correct  
F. S.

**The Helium in Recent Minerals.** ARNALDO PIUTTI (*Le Radium*, 1910, 7, 178—179).—Other investigators previously have not detected helium in the strongly radioactive minerals carnotite, torbernite, and autunite (compare Bordas, *Ahstr.*, 1908, ii, 505).

With the apparatus described in a previous paper (*Le Radium*, 1910, 7, 142), the spectrum of helium was clearly detected in the two first, but not in the last, quantities of 3 grams being employed. The limit of detection is given as 0.036 cu. mm. of helium. In the very interesting cases of minerals, which are strongly radioactive, formed in contemporaneous eruptions of Vesuvius, the presence of helium could not be detected. The activity of the minerals formed in the eruption of 1906 (cotunnite and galena) has been shown to be due to radium-D, -E, and -F only, and it is reasonable to draw the conclusion that sufficient time has not elapsed for a detectable quantity to have accumulated. In galena from the more ancient lava of Monte Somma, neither helium nor radioactivity could be detected, nor in titanite (0.32 gram) from Ischia, which was radioactive. F. S.

**The Density of the Radium Emanation.** SIR WILLIAM RAMSAY and ROBERT WHYTLAW GRAY (*Compt. rend.*, 1910, 151, 126—128).—The volume of the emanation used has been calculated from the value previously found for the volume in equilibrium with 1 gram of radium (0.601 cu. mm.), and in no case exceeded 0.1 cu. mm. This was weighed sealed up in a small capillary tube on a quartz balance of which the sensitiveness exceeds the half-millionth of a milligram (compare Steele and Grant, *Ahstr.*, 1909, ii, 876), in which the pressure of the air in the balance case was adjusted, and the buoyancy of a small sealed quartz bulb containing air used instead of weights. The tip of the capillary was then broken, and its weight again taken. Five measurements of the density are given, in which the weight of the emanation found was of the order of  $6 \times 10^{-7}$  gram, and values for the molecular weight between 216 and 228 were obtained. The mean value was 220. There is now therefore no doubt that the true atomic weight is 222.5, as deduced from the disintegration theory by subtracting from the atomic weight of radium 226.5, the weight of the atom of helium 4 expelled as an  $\alpha$ -particle. To put the radium emanation in its proper place as the second member in the series of inactive gases after xenon, the name *Niton*, symbol Ni, is proposed. F. S.

**The Slow Precipitation of Radium Sulphate.** LÉON KOLOWRAT (*Le Radium*, 1910, 7, 157—159).—A series of experiments has been made with a dilute solution of pure radium chloride after addition of sulphuric acid and filtration, to investigate the slow continuous diminution in the rate of production of emanation in the solution observed by Mme. Curie. It was found that after some weeks, when the rate of production had fallen to about one-half the initial value, heating to 70° before the test increased the amount of emanation evolved enormously. Heating and removal of the emanation before the time of accumulation for the test resulted in a nearly normal result. In a series of tests in which the temperature at

the test was lower than at the preceding test, the quantity of emanation steadily diminished. The results obtained agree quantitatively with the view that an invisible precipitate of radium sulphate slowly forms in the solution, and from this precipitate the emanation is not all liberated, but accumulates. On heating the emanation is obtained, not only from the solution, which is formed during the period of accumulation between the tests, but also from that part of the precipitate, soluble at the higher, but insoluble at the lower temperature, which has been accumulating since the precipitate was formed. There is therefore no necessity for supposing that a new member exists, intermediate in the series between radium and its emanation (radium- $X$ ). A perfect analogy exists between the phenomena observed in solutions and in solids (Kolowrat, this vol., ii, 91).

F. S.

**The Constituents of the Induced Activity of Actinium.**  
Mlle. L. BLANQUIES (*Compt. rend.*, 1910, 151, 57—60; *Le Radium*, 1910, 7, 159—162. Compare Abstr., 1909, ii, 634).—Further experiments are described to test the view that the  $\alpha$ -rays of actinium- $B$  are complex and derived from two consecutive changes. The supposed product of actinium- $B$  is termed actinium- $B'$ . The active deposit of actinium electrolysed in hydrochloric acid solution gave on the cathode a product decaying rather more rapidly during the first minute than would be the case if it consisted of actinium- $B$ . The effects observed were small, but a period of about 2.25 minutes is attributed to the new substance. The recoil product from the active deposit consists mainly of actinium- $C$  with some actinium- $A$ . It decays at first rather more rapidly than the latter, which may be due either to actinium- $B'$  recoiling from actinium- $B$ , or to the latter removed mechanically like actinium- $A$ , so this evidence is equivocal. The scintillations produced by the active deposit placed at a fixed distance from the zinc sulphide screen, the pressure of the gas in the apparatus being varied, were compared with those produced by polonium.

At a pressure 1 cm. below that which caused the scintillations to disappear, increase of pressure caused between two and three times more rapid diminution of the number of scintillations in the case of actinium than in that of polonium. This is well in agreement with what is to be expected on the view under consideration. The analogy between actinium and thorium, and the large proportion of double scintillations observed with the active deposit of actinium (compare Geiger and Marsden, this vol., ii, 92), also supports the view, although it has not been possible to obtain as yet any complete proof of its correctness.

F. S.

**Radioactivity of the Mineral Springs of Switzerland.**  
**Emanation Content of the Water.** II. ALFRED SCHWEITZER (*Arch. Sci. phys. nat.*, 1910, [iv], 30, 46—66. Compare Abstr., 1909, ii, 363).—The previous investigations have been continued on many new springs with improved apparatus, designed for use with hot waters, in which the latter are contained during measurement in an

hermetically closed vessel. Three new springs containing notable quantities of emanation have been found. One in the Val Luthpègnia, near Disentis, had an activity of 9.16 Machs units. The other two were Spring No. 2 of Gränichen (7.56), and the "Satro" spring at Acquarossa (5.17).  
F. S.

The Exclusive Presence in Gases Derived from Certain Hydrogen Flames of Ions Completely Analogous (in Mobility) to those Produced by Röntgen Rays. MAURICE DE BROGLIE (*Compt. rend.*, 1910, 151, 67—68. Compare *ibid.*, 150, 1425).—With proper precautions, numerous hydrogen flames produce only small ions, which previously had been observed only for the carbon monoxide flame. The combustible gas, well filtered and dried, is diluted with nitrogen and burnt with a very small flame at the foot of a lead tube inside a very dry tube carefully cooled with cold water. The flames employed consisted mainly of hydrogen, ethyl ether, acetaldehyde, acetone, and pentane, whilst illuminating gas continued in these circumstances still to give ions of feeble mobility. The mobility of the small ions was between 0.75 and 1 in terms of that of those given in ordinary circumstances by X-rays or radium. The results indicate that chemical action and high temperature together produce small ions, which in absence of precautions are transformed into large ions by condensation, solid walls in the neighbourhood of the flame as well as water vapour being necessary. The results explain those of von Helmholtz on the efficacy of different flames to condense a steam jet, the ether flame producing scarcely any effect, and even being cited as not giving ionisation. This is due to the small ions being far less active in promoting condensation than the large ions, and to their rapid recombination rendering the conductivity of the gas more ephemeral.  
F. S.

Conduction of Electricity in Mixtures of Metals and their Salts. II and III. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1910, 73, 578—597, 624—637. Compare Abstr., 1909, ii, 537).—II. The electrical conductivity of fused mixtures of cadmium and cadmium chloride at 580°, 600°, and 620° has been determined by the method already described (*loc. cit.*). The conductivity of the mixtures increases rapidly as the temperature is raised, whilst the addition of cadmium to fused cadmium chloride progressively lowers the specific conductivity.

This lowering may be due to the absence of any passage of electrons from metal to solution or to the very small velocity of the electrons in the mixture; in the first case the dissolved metal should have no conductivity, and in the latter case its conductivity should be of the same order as that of an electrolyte. In connexion with this point, the density of the mixtures of cadmium chloride and metal has been determined at 600°. The density of the chloride at this temperature is 5.299. The available data show that the conductivity of the dissolved metal is very small, much smaller than that of the chloride, and it may be zero; they do not, however, serve to decide conclusively between the two views as to the effect of the metal.

Freezing-point determinations with mixtures of cadmium chloride and cadmium appear to show that no compound of the formula  $\text{CdCl}$  separates from the fused mass, and this view is supported by microscopic observations. The compound  $\text{CdCl}$  may, however, exist in the fused mixture.

III. Equations are deduced which show the influence of different factors on the validity of Faraday's law for the electrolysis of a mixture of cadmium chloride saturated with metallic cadmium. It is shown that if the mixture has no metallic conductivity and no complex formation takes place, more metal will pass into solution than corresponds with Faraday's law. This deviation will be increased if complex formation between  $\text{CdCl}_2$  molecules and anions or electrons occurs, and also if the dissolved metal is partly present in the form of a subchloride.

Experiment shows that for 1 equivalent of silver, 0.83 equivalent of cadmium is dissolved or set free, so that either metallic conductivity or complex formation, or both, must occur. Although the data are not sufficient to decide the question conclusively, the deviation from Faraday's law appears too great to be accounted for by metallic conductivity alone. G. S.

Reactions in the Iron-Nickel Peroxide Accumulator.  
III. Behaviour of the Iron Electrode. FRITZ FOERSTER and VIKTOR HEROLD (*Zeitsch. Elektrochem.*, 1910, 16, 461—498).—The study of the nickel peroxide electrode (Abstr., 1908, ii, 146, 147, 558) is now completed by a very exhaustive investigation of the iron electrode. Faust (Abstr., 1907, ii, 426) found that the iron electrode is discharged in two (possibly three) stages. The authors have studied these both analytically and electrically. The potentials of the iron electrode are referred to the normal hydrogen electrode, compared with which the iron is negative. Faust used zinc in 20% potassium hydroxide as a standard electrode; its potential compared with the hydrogen electrode is  $-1.27$  volt, which makes it possible to compare Faust's measurements with those in the present paper.

The electrodes were made by pressing a mixture of finely divided iron and graphite into the perforated steel cells used by Edison in his accumulator. An impalpable iron powder is obtained by Edison's process by reducing a fine-grained ferric oxide with hydrogen at about  $480^\circ$ , and then drowning it in water, by which treatment it loses its pyrophoric properties owing to a surface oxidation. A more coarse-grained powder was also used. The metallic iron in these powders is estimated by boiling with mercuric chloride, which dissolves the metal, but has no action on ferrous or ferric oxide.

When an electrode is first made, the iron is passive (2.85N-potassium hydroxide solution is the electrolyte used throughout the experiments), but a very small quantity of occluded hydrogen is sufficient to make it active. This hydrogen charge may be given to the iron either by cathodic polarisation or by treatment with an acid or a neutral solution of ferrous sulphate. The potential of the electrode (at  $18^\circ$ ) is  $-0.87$  to  $-0.88$  volt, and during the first stage of the discharge it remains near this value. The chemical change which occurs is the

conversion of iron into ferrous hydroxide. The ferrous hydroxide forms a film round each particle of iron, which prevents its contact with the electrolyte; the charge of hydrogen is therefore soon oxidised and cannot be replaced by the interaction of electrolyte and iron, and the latter becomes passive. The second stage now sets in, the chemical reaction supplying the current being the oxidation of ferrous to ferric hydroxide. The potential of an electrode consisting of graphite and ferrous hydroxide is  $-0.74$  to  $-0.76$  volt, which is also the potential of the iron electrode in the second stage of the discharge. During this stage, iron reacts with the ferric hydroxide, forming ferrous hydroxide, so that the analyses of the electrode show that iron disappears and ferric hydroxide is formed. The effect of adding mercury to the iron powder (in the recent forms of the Edison accumulator) is studied. The effect is to increase the capacity of the first stage by keeping the iron in the active state longer than is the case without mercury. In charging the electrode, the ferric hydroxide is reduced quantitatively, but the ferrous hydroxide is only reduced slowly, so that a large quantity of hydrogen is evolved and the efficiency of the electrode is far from theoretical. Since the oxidation of the iron in discharging the electrode is only superficial, it is necessary, in order to get considerable capacity, to use the iron in the most finely divided form that can be obtained.

T. E.

The Rectilinear Diameter for Oxygen. ÉMILE MATHIAS and HEIKE KAMERLINGH ONNES (*Compt. rend.*, 1910, 151, 213—216. Compare Abstr., 1909, ii, 552).—A discussion of the surface representing the state of gases at the critical temperature, with an account of the method employed in the case of oxygen to determine whether the diametral line is rectilinear for a gas having a very low critical temperature.

W. O. W.

Absorption of Gases by Charcoal. IDA F. HOMFRAY (*Proc. Roy. Soc.*, 1910, 84, A, 99—106 \*).—The apparatus employed was of the nature of a gas thermometer; the bulb contained 3 grams of charcoal, and the equilibrium pressures exerted at different temperatures after the admission of successive volumes of a gas were measured. Experiments were made with helium, argon, nitrogen, carbon monoxide, methane, ethylene, carbon dioxide, and oxygen, as well as with mixtures of carbon monoxide and nitrogen, and the temperatures of observation extended from that of liquid air to the boiling point of aniline.

The measurements were first represented on isothermal and isobaric diagrams, and from these, points of equal absorption were read off and curves, so called "isosteres," plotted, having pressures as ordinates, and absolute temperatures as abscissæ. The concentration by weight,  $C$ , for each isostere is calculated in the form  $C = 100w/(W + w)$ , where  $w$  = weight of gas absorbed in  $W$  gramme of charcoal.

The following two relationships have been found to hold: (1) at constant concentration  $T_0/T_1 - T'_0/T'_1 = R(T_0 - T'_0)$ , where  $T_1$  and  $T'_1$  are the absolute temperatures read from any one isostere at any two pressures,  $T_0$ ,  $T'_0$  are the absolute temperatures at which any saturated vapour

\* and *Zeitsch. physikal. Chem.*, 1910, 74, 129—201.



taken as standard has the same pressures, and  $K$  is a constant; (2) at constant pressure:  $-dT/(d \log C) = K$ . From these two relations, if the vapour-pressure curve of a liquefied gas is known, together with three values of temperature, pressure, and concentration in the presence of charcoal, the whole absorption diagram can be mapped. The values of  $dT/(d \log C)$  for the different gases at the same pressure increase uniformly with increasing complexity of molecular structure from argon to ethylene.

From the isosteric curves, the molecular heat of absorption,  $\lambda_r$ , can be calculated by the thermodynamical formula:  $\lambda = 2T^2 d \log_e P/dT$ . A simple method of calculating the results is described, and the applicability of the formula has been shown by direct calorimetric measurements with carbon dioxide at atmospheric temperature.

The absorption curve for mixtures of nitrogen and carbon monoxide is found to lie between those for the single gases at all compositions. From this result, certain deductions are made which may be of value in separating mixed gases by selective absorption in charcoal.

The nature of absorption is discussed. Objections are advanced to explanations on the basis of chemical combination or surface condensation, and a solution hypothesis is favoured. The fundamental objection to the latter explanation is that Henry's law does not hold for the distribution between gas space and charcoal, but in the present case the solutions are by no means dilute, and the deviations from the simple laws appear to be analogous to those shown by concentrated solutions.

G. S.

**Adsorption of Iodine by Solids.** MARCEL GUICHARD (*Compt. rend.*, 1910, 151, 236—238. Compare Abstr., 1909, ii, 136).—Attention has previously been called to the persistence with which iodic anhydride retains iodine. A table is now given, showing for silica and the oxides of aluminium, magnesium, and glucinum in different physical states the amount of iodine adsorbed and the length of time required for saturation. Oxides prepared by calcination at a high temperature, and having a density approaching the limit, take up only traces of iodine. Carbon heated at 600° adsorbs 34.2% at the ordinary temperature.

W. O. W.

**Dimorphism and Mixed Crystals occurring in Liquid-Crystalline Substances.** Applications of the Phase Rule. OTTO LEHMANN (*Zeitsch. physikal. Chem.*, 1910, 73, 598—623).—Largely polemical against Prins (compare Abstr., 1909, ii, 869) and Schenck (*Krystallinische Flüssigkeiten*, Leipzig, 1905, etc.), and is partly concerned with questions of priority. With reference to some of the points in dispute, the transition and saturation temperatures for mixtures of cholesteryl decanoate and *p*-azoxyanisole have been determined by means of the author's crystallisation-microscope, and the results are figured and described in detail.

G. S.

**Validity of the Boyle-Gay-Lussac Laws for Colloidal Solutions.** THE SVEDBERG (*Zeitsch. physikal. Chem.*, 1910, 73, 547—556. Compare Abstr., 1909, ii, 277, 561, 723).—The number

of visible particles in a definite volume of a colloidal solution observed under the ultramicroscope varies, owing to Brownian motion. If  $n$  is the momentary value observed,  $n_1$  the number of gas-molecules which would be present in this volume if the distribution were uniform, and  $\delta = (n - n_1/n_1)$  is the mean deviation when all the positive and negative deviations are taken into account, then, as shown by von Smoluchowski (*Ann. Physik*, 1908, [iv], 25, 205),  $\bar{\delta} = \sqrt{2/n_1\pi}$  if  $n_1$  is a large number, and  $\bar{\delta} = 2n_1^k e^{-n_1}/k!$  when  $n_1$  is a small number, provided that the gas laws are valid for the solution. In the last formula,  $k$  is the greatest whole number less than or equal to  $n_1$ . If the gas laws do not apply, then  $\bar{\delta} = \sqrt{2/n_1\pi} \sqrt{\beta/\beta_0}$  when  $n_1$  is a large number ( $\beta$  is the actual compressibility, and  $\beta_0$  the compressibility, provided the gas laws hold). If  $n_1$  is a small number, then  $\bar{\delta} = (2n_1^k e^{-n_1} \sqrt{\beta/\beta_0})/k!$  approximately.

The author has counted the particles in a limited volume of solution of colloidal gold and in one of colloidal mercury under the ultramicroscope, and finds on applying the above formulae that the gas laws apply to dilute solutions, but the observed osmotic pressures are greater than the theoretical values in relatively concentrated solutions.

G. S.

**Some Presumed Chemical and Physical Effects of Pressure Uniform in all Directions.** GIORGIO SPEZIA (*Atti R. Accad. Sci. Torino*, 1910, 45, 525—538).—If fine filings of copper or silver are enclosed in a steel cylinder under a pressure of 8000 atmospheres for a month at the ordinary temperature, apparently homogeneous cylinders are obtained, as described by Spring. Microscopical examination shows, however, that the filings are still distinct, and are merely united by adhesion, no molecular interpenetration having taken place. Similarly, a mixture of copper and silver filings yields a cylinder in which the original silver and copper particles are clearly distinguishable. It is improbable that the diffusion would take place if longer time were allowed, as a microscopical examination of the native copper of Keveanaw Point, in which inclusions of silver occur, shows that diffusion has not occurred to any measurable extent during a geological epoch.

Experiments with lead and wax under a pressure of 9,900 atmospheres at 15°, continued for twelve days, show that the lead does not behave as a fluid under such conditions. There is thus a complete difference between the effects of pressure uniform in all directions and of pressure causing flow through an orifice, and there is no reason to assume that pressure of the former type produces any plasticity or increases diffusion. There is no tendency for a cylinder or prism, subjected to pressure uniform in all directions, to assume a spheroidal form. In the experiments of Spring and Kahlbaum, the diminution of density observed under high pressures is to be attributed to inequalities in the distribution of pressure, producing deformation.

C. H. D.

**Periodicity of the Properties of the Elements. New Arrangement.** JAMES F. TOCHER (*Pharm. J.*, 1910, [iv], 31, 159—160).—The

elements are arranged in a logarithmic spiral. The radius vector,  $r$ , in three-dimensional space, is a function of the atomic weight and of the atomic volume of each element. The vectorial angle is a function of the valency of an element; it has a constant value,  $\theta = \pi/8$ , and in the spiral is the angle between two adjacent radii, one with an element  $E_n$  and the other with an element  $E_{n+1}$  with next higher atomic weight.

The figure of a model is given, in which the atomic weight of each element is shown as a length on the  $xy$  plane, and the atomic volume as a height on the  $zz$  plane. If valency is defined as the combining power of an element with hydrogen, the valency varies as  $\sin \theta$ , being zero along the  $x$  axis, on which lie the inert gases, and attaining a maximum at  $90^\circ$  and at  $270^\circ$ . The first or upper right-hand quadrant contains the electro-negative elements, the heavy and the noble metals are situated mainly in the second quadrant, the rarer elements mainly in the third quadrant, whilst the fourth quadrant contains the alkali metals and other strongly positive elements. The scheme can only be appreciated by reference to the model.

C. S.

## Inorganic Chemistry.

**Nitrous Oxide.** I. ALFRED STAVENHAGEN and E. SCHUCHARD (*Ber.*, 1910, 43, 2171—2174).—When sulphur is strongly heated in a stream of nitrous oxide, it burns with a brilliant bright greenish-blue flame. If the combustion is carried out in a large glass vessel, the walls become covered with crystals of nitrosulphonic acid, and at the same time nitrogen peroxide is formed in quantity.

Thus nitrous oxide may be transformed into higher oxides of nitrogen without the use of electrical energy by simply burning sulphur in it, nitrosulphonic acid anhydride or its decomposition products being formed at the same time.

T. S. P.

**Acceleration of the Reduction of Quinquevalent Arsenic by Hydrogen Bromide. A Correction.** MARTIN ROEMER (*Ber.*, 1910, 43, 2262).—The method described by Jannasch and Seidel (this vol., ii, 546) for the reduction of quinquevalent arsenic by means of potassium bromide or hydrobromic acid has been known for nine years (compare *Abstr.*, 1901, ii, 194), and during that time has often been recommended in the scientific literature and in patent specifications as a catalyst for reducing actions.

T. S. P.

**Percarbonates.** SEBASTIAN M. TANATAR (*Ber.*, 1910, 43, 2149—2151).—The author confirms Riesenfeld's observations (this vol., ii, 290) that in solutions of the same alkalinity potassium percarbonate liberates more iodine from potassium iodide than does sodium percarbonate, but points out that this is only true when solid

potassium percarbonate is used, or a freshly-prepared solution of the same. A solution of the potassium salt which has been made for five minutes reacts similarly to sodium percarbonate. It follows that potassium percarbonate liberates iodine quicker than it undergoes hydrolysis, since as soon as hydrogen peroxide is present in the solution the iodine is decolorised.

Riesenfeld has not taken into account the fact that a solution containing 1 mol. of sodium percarbonate,  $(\text{Na}_2\text{CO}_3)_2\text{H}_2\text{O}_2$ , contains  $\frac{1}{2}$  mol. of hydrogen peroxide from the commencement, and thus the liberation of iodine is hindered.

The author considers that hitherto no reaction has been discovered which distinguishes with certainty per-salts from salts containing hydrogen peroxide of crystallisation. T. S. P.

**The Ternary System: Sodium Sulphate-Sodium Fluoride-Sodium Chloride.** ADOLF WOLTERS (*Jahrb. Min. Beil. Bd.*, 1910, 30, 55—95).—The thermal and optical investigation of the systems sodium sulphate-sodium chloride and sodium sulphate-sodium fluoride has been re-investigated, as also has the system sodium chloride-sodium fluoride. None of the three components forms mixed crystals with either of the other components.

In the system sodium sulphate-sodium fluoride the compound  $\text{Na}_2\text{SO}_4 \cdot \text{NaF}$  is formed. It is enantiotropic-dimorphic, the transition temperature being  $105^\circ$ . Microscopical investigation showed it to be mimetic-hexagonal at the ordinary temperature, and truly hexagonal at higher temperatures. The double refraction is positive.

The refractive index of sodium fluoride for sodium light is 1.3255.

A theoretical discussion of the cooling curves and freezing-point phenomena of ternary systems is given. The ternary system sodium sulphate-sodium fluoride-sodium chloride is very simple, there being no complications, with the exception of the transformations mentioned above. The four solid phases, including the double salt, are not miscible with each other at all.

A compound corresponding with the mineral sulphohalite could be obtained neither from the fusions nor from aqueous solutions.

T. S. P.

**Constitution of Sodium Hydrogen Carbonate.** BICNER (*Chem. Zeit.*, 1910, 34, 765—766).—The author considers that the ordinary formula assigned to sodium hydrogen carbonate is incorrect, since when it is calculated with the formation of the normal carbonate the temperature is such that it cannot be supposed that the sodium atom of one molecule displaces the hydrogen atom of another molecule, the substances being in the solid state. The formula should therefore be written as  $(\text{NaHCO}_3)_2$ , or, better, as  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{CO}_3$ , a double salt of sodium carbonate and carbonic acid.

This formula is used to explain the ease with which sodium hydrogen carbonate loses carbon dioxide, and the action of ammonia, barium chloride, and lime respectively on the aqueous solutions. Equations are also given for the ammonia soda process. T. S. P.

**Method for the Preparation of Stable Colloidal Metals.** CESARE SERONO (*Arch. Farm. experim.*, 1910, 9, 152—157).—Stable colloidal solutions of certain metals may be obtained by electrolysing a solution of pure gelatin, rendered slightly conducting by an alkali chloride or sulphate, between metallic electrodes.

A 5% solution of gelatin is used, containing 1% of sodium chloride or sulphate, and contained in a glass vessel. The anode is placed in this vessel, whilst the cathode, composed of the metal to be rendered colloidal, is enclosed in an inner porous cell. A continuous current of 3 to 5 amperes is used at 120 volts. Considerable foaming takes place, and it is necessary to interrupt the operation from time to time to prevent loss of liquid. After about ten minutes, a colloidal solution of the metal is obtained in the neighbourhood of the anode. The liquid surrounding the cathode is free from metal.

In the case of gold, a violet colloidal solution is obtained containing 42 mg. of gold per litre. It is clear by transmitted, but opalescent by reflected, light, and is very stable, remaining unchanged in air for more than a month, the gold preserving the gelatin in a perfectly sterile condition. A similar colloidal solution of silver is obtained, containing 87 mg. of silver per litre. Iron yields a solution containing a ferrous salt, together with colloidal iron, and a small precipitate of ferrous hydroxide. By the prolonged action of the current, large quantities of metal may be brought into solution, in one case 3.225 grams of silver being dissolved in 448 c.c. of liquid.

It is assumed that, in the electrolysis of sodium chlorides with gold electrodes, the chlorine liberated attacks the gold anode, forming gold chloride, and that the gelatin is partly decomposed, yielding acids resembling protalbic and lysalbic acids, which then reduce the gold to the colloidal metallic state, as in Paal's method of preparation.

C. H. D.

**Binary Systems Formed from the Alkali Sulphates and Calcium Sulphate.** HANS MÜLLER (*Jahrb. Min. Beil. Bd.*, 1910, 30, 1—54).—The normal sulphates of potassium, rubidium, and cesium are enantiotropic-dimorphic, being rhombic at the ordinary temperature and hexagonal at higher temperatures. Twin crystals separate from the fusion, but twinning disappears at the transition point. With rising temperature, expansion takes place at the transition point, and the cubical coefficient of expansion of the rhombic modification is greater than that of the hexagonal. The melting points are:  $K_2SO_4 = 1057^\circ$ ,  $Rb_2SO_4 = 1051^\circ$ ,  $Cs_2SO_4 = 995^\circ$ , and the transition points are respectively:  $580^\circ$ ,  $649^\circ$ , and  $660^\circ$ . The latent heat of fusion decreases very slightly from potassium sulphate to cesium sulphate, whereas the latent heat of transition decreases very greatly in the same order, being practically zero for cesium sulphate.

The temperature-concentration diagrams of the systems composed of calcium sulphate with potassium sulphate, rubidium sulphate, sodium sulphate, lithium sulphate, rubidium sulphate, and cesium sulphate respectively were determined both thermally and optically, with the following results. The double salt,  $K_2SO_4 \cdot 2CaSO_4$ , exists; it is enanti-

tropic-dimorphic, the transition temperature being  $936^{\circ}$ , and m. p.  $1004^{\circ}$ . It takes up water with the formation of a hydrate containing  $\frac{1}{2}\text{H}_2\text{O}$ .

Rubidium and calcium sulphates form the enantiotropic-trimorphic double salt,  $\text{Rb}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ , m. p.  $1043^{\circ}$ . The first transition point is at  $915^{\circ}$ , the second at  $787^{\circ}$ .

The double salt,  $\text{Cs}_2\text{SO}_4 \cdot 2\text{CaSO}_4$ , was obtained from the fusions. It is dimorphic, with m. p.  $959^{\circ}$ , and a transition temperature of  $722^{\circ}$ . Pure sodium sulphate has a transition temperature at  $233^{\circ}$ , contraction taking place when the transformation takes place with rising temperature. With calcium sulphate, it forms the double salt,  $4\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ , which is completely miscible with sodium sulphate, and exists in one doubly refracting modification only. It takes up water, forming a hydrate with  $1\text{H}_2\text{O}$ .

Glauberite cannot be prepared by the fusion method. From a fusion having the composition of glauberite, anhydrite is first deposited, the remainder then solidifying as a eutectic of anhydrite and mixed crystals of  $\text{CaSO}_4 \cdot 4\text{Na}_2\text{SO}_4$  with  $\text{CaSO}_4$ .

Lithium sulphate and calcium sulphate form neither double salts nor mixed crystals.

The double salt,  $\text{Rb}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ , is enantiotropic-dimorphic; m. p.  $730^{\circ}$ , and transition temperature of  $142^{\circ}$ . The double salt,  $\text{Cs}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ , exists in one modification only, m. p.  $729^{\circ}$ .

General conclusions to be drawn are as follows. It is not always possible to determine the temperature-concentration diagram by thermal methods alone, since (a) the heat of transformation is at times so small that the cooling curve does not show an arrest. This is the case, for example, with  $\text{Cs}_2\text{SO}_4$  and  $\text{Rb}_2\text{SO}_4 \cdot \text{Li}_2\text{SO}_4$ . (b) Owing to the formation of mixed crystals, the transformation is often so retarded, or spread over so great an interval, that it is not noticeable thermally. This is the case with the system  $\text{Na}_2\text{SO}_4$ - $\text{CaSO}_4 \cdot 4\text{Na}_2\text{SO}_4$ . (c) When the fusion curve runs very close to the eutectic line only one arrest is obtained on the cooling curve; for example: the system  $\text{CaSO}_4 \cdot 4\text{Na}_2\text{SO}_4$ - $\text{CaSO}_4$ .

Optical investigations do not always lead to conclusive results, since in some cases thin sections of fusions from which one component has separated first cannot be distinguished from sections of the eutectic; in other cases, from a fusion of eutectic composition the one component may separate without, and the other with, super-cooling. The latter then appears as an older, pre-eutectic formation.

T. S. P.

**Deposition of Calcium Carbonate from Solutions of Calcium Hydrogen Carbonate.** F. VETTER (*Zeich. Kryst. Min.*, 1910, 48, 45—109).—The author has studied the deposition of calcium carbonate from solutions of calcium hydrogen carbonate in (1) pure water; (2) sea-water containing 27.90 grams of  $\text{NaCl}$ , 2.34 grams of  $\text{MgCl}_2$ , 1.55 grams of  $\text{KCl}$ , 0.52 gram of  $\text{NaBr}$ , 1.56 grams of  $\text{CaSO}_4$ , 1.85 grams of  $\text{MgSO}_4$ , in 1000 grams of water; (2a) sea-water plus 2.03 grams of ammonium sulphate per litre. Also from solutions containing in 1000 grams of water (a) 1.56 grams of calcium sulphate, (b) 27.90 grams of sodium chloride, (c) 1.85 grams of magnesium sulphate, (d) 2.34 grams of magnesium chloride, (e) 1.55 grams of

potassium chloride, (f) 20.74 grams of ammonium chloride (equivalent to 27.90 grams of sodium chloride), (g) 2.03 grams of ammonium sulphate (equivalent to 1.8 grams of magnesium sulphate), (h) a saturated solution of sodium chloride.

The solutions were saturated with calcium hydrogen carbonate under a pressure of 1 atmosphere of carbon dioxide. Eighty to 120 c.c. of these solutions were used in each experiment, and the calcium carbonate was deposited by drawing dust-free air through them for one and a-half to two hours. In some cases, nuclei of aragonite or calcite were added. The temperatures varied from  $0^{\circ}$  to  $55.5^{\circ}$ . Experiments were also made in which the deposition was brought about by first drawing air charged with ammonia through the solutions for one to two minutes, and then air alone.

In sea-water, nuclei of aragonite do not favour the deposition of that substance; in no case was aragonite alone deposited. They apparently hinder the deposition of hydrated calcium carbonate ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ), except in one case each from solutions of magnesium sulphate and chloride. From pure calcium hydrogen carbonate solutions they favour the deposition of aragonite, although their influence is not very marked. The calcite deposited in the presence of aragonite nuclei never occurs in the form of spheruliths and axioliths, although in the absence of these nuclei it is deposited preferably in these forms.

Nuclei of calcite have a very great effect and hinder, or very much limit, the deposition of unstable forms. From sea-water at  $0^{\circ}$ , the presence of calcite nuclei does not always prevent the deposition of Vater's modification (*Zeitsch. Kryst. Min.*, 1893, 21, 433) and of the exceedingly unstable compound,  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ .

The formation or greater stability of aragonite, Vater's modification, and hydrated calcium carbonate in sea-water is not due so much to the salt content as to the presence of magnesium salts. It is improbable that hydrated calcium carbonate plays any part in natural processes. Owing to the unfavourable solubility relations and to the slow establishment of equilibrium, the acceleration of the deposition of calcium carbonate from calcium hydrogen carbonate solutions is of very little importance so far as the formation of metastable modifications is concerned.

T. S. P.

**Carbides of Magnesium.** I. J. Novák (*Zeitsch. physikal. Chem.*, 1910, 73, 513—546. Compare Abstr., 1909, i, 865).—Magnesium was heated in a tube at a definite constant temperature, and a definite volume of a gaseous hydrocarbon passed over it. The products obtained in different experiments were decomposed by water, the acetylene converted into cuprous acetylido, the allylene into the silver compound (compare Berthelot, *Ann. Chim. Phys.*, 1866, [iv], 9, 423), and from the relative amounts of these gases the composition of the residue was determined. It is shown that two carbides of magnesium,  $\text{MgC}_2$  and  $\text{Mg}_2\text{C}_3$ , exist; they are decomposed by water according to the equations:  $\text{MgC}_2 + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{C}_2\text{H}_2$  and  $\text{Mg}_2\text{C}_3 + 4\text{H}_2\text{O} = 2\text{Mg}(\text{OH})_2 + \text{C}_2\text{H}_2$ .

The decomposition of acetylene, accompanied by the formation of the carbide,  $\text{MgC}_2$ , begins about  $400^{\circ}$ ; the proportion of the carbide

increases rapidly up to  $490^{\circ}$ , and beyond that point diminishes. Even at  $700^{\circ}$ , however, this carbide can still be detected in the reaction product. At  $460^{\circ}$  the presence of the carbide,  $Mg_2C_3$ , in the product can be proved; the proportion increases regularly up to  $545^{\circ}$ . At  $714^{\circ}$ , a large proportion of carbon is produced, and soon blocks up the tube. The products obtained between  $465^{\circ}$  and  $515^{\circ}$  are hard, compact masses, steel-grey in colour, and only decompose water slowly; those obtained above  $550^{\circ}$  are grey, brittle, and rapidly decompose water. The proportion of free carbon, formed by heating in a steel tube, is greater than when a porcelain tube is used, as in the above experiments.

With methane, the proportion of the carbide,  $Mg_2C_3$ , to free carbon produced is at first great, and only at  $780^{\circ}$  is the proportion of carbon the greater. The maximum point for the formation of  $Mg_2C_3$  is  $780^{\circ}$ . The other carbide,  $MgC_2$ , could only be detected at  $733^{\circ}$ . The results with pentane and with octane are very similar to those with methane; the maximum in the formation of the carbide,  $Mg_2C_3$ , occurs in both cases about  $700^{\circ}$ . Of these three hydrocarbons, octane begins to decompose at the lowest temperature.

The results with benzene, toluene, and the three xylenes are somewhat similar to those for the three paraffins. In all cases the proportion of the carbide,  $MgC_2$ , is small, and the maximum formation of  $Mg_2C_3$  occurs at temperatures ranging from  $650^{\circ}$  to  $720^{\circ}$ . The decomposition of toluene begins at the lowest temperature,  $520^{\circ}$ .

The relative proportions of the carbides and free carbon produced under different conditions are explained by the fact that at temperatures in the neighbourhood of  $570^{\circ}$ , the reaction  $2MgC_2 \rightarrow Mg_2C_3 + C$  is fairly rapid; this reaction predominates up to  $610^{\circ}$ , above which temperature the further reaction  $Mg_2C_3 \rightarrow Mg_2 + 3C$  becomes of most importance. The effect of temperature on the stability of the carbides is illustrated graphically.

G. S.

[The Alloys of] Copper, Antimony, and Bismuth. NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 835—840).—Antimony and bismuth appear to form a continuous series of solid solutions, and an alloy containing 80% Bi, which, when first prepared, contains two structural constituents, becomes practically homogeneous after heating for ten days at  $320^{\circ}$ . Antimony does not retain copper in solid solution, the eutectic being distinctly present in an alloy containing 15% of copper. Copper does not retain more than a very minute quantity of antimony in solid solution. The ternary system is to be described.

C. H. D.

New Compounds of Quadrivalent Cerium. GIUSEPPE A. BARBIERI and J. CALZOLARI (*Ber.*, 1910, 43, 2214—2216).—Ceric salts may be obtained by oxidation of cerous salts with nitric acid when the acid of the cerous salt is non-volatile and does not react with nitric acid (compare Barbieri, *Abstr.*, 1907, ii, 466). In this way *ceric selenite*,  $Ce(SO_3)_2$ , *ceric dihydrogen arsenate*,  $Ce(H_2AsO_4)_2 \cdot 4H_2O$ , and *ceric monohydrogen arsenate*,  $Ce(HAsO_4)_2 \cdot 6H_2O$ , have been prepared.

*Ceric selenite* is prepared by heating 10 grams of cerous nitrate hexahydrate and 12 grams of selenious acid with 200 c.c. of nitric acid



(D 1'40) under reflux for some hours. It is an orange-yellow powder, insoluble in water, but slightly soluble in concentrated nitric acid.

*Ceric dihydrogen arsenate* is formed by heating cerous nitrate (1 mol.) and arsenic acid (4 mols.) with concentrated nitric acid for some hours. After distilling off the excess of nitric acid, the pale yellow solution deposits white needles of the above salt. When it is dissolved in the minimum quantity of concentrated nitric acid and the cold solution diluted with water, a white, crystalline deposit of *ceric monohydrogen arsenate* is formed, arsenic acid remaining in solution. T. S. P.

**Thermic Reduction of Alumina.** PAUL ASKENASY and A. LEBERDEFF (*Zeitsch. Elektrochem.*, 1910, 16, 559—566).—As previous observers have obtained contradictory results on the reduction of alumina by carbon, a complete review of the literature is given. The authors have made experiments with direct and alternating current arc furnaces and with an electrical resistance furnace. A mixture of alumina and wood charcoal heated in an arc furnace (similar to those employed in making calcium carbide) gives off large quantities of carbon monoxide at first followed by brilliant flames of burning aluminium vapour. If the heating is stopped as soon as these appear, the product consists of fused alumina mixed with aluminium carbide and aluminium. In the carbon tube resistance furnace, the highest temperature reached was not much above the melting point of alumina (about 2000°), and here, too, both carbide and metal were formed. Aluminium carbide is not changed when heated in a vacuum at any temperature between 400° and 1400°. The authors think that aluminium carbide is first formed:  $2\text{Al}_2\text{O}_3 + 9\text{C} = \text{Al}_4\text{C}_3 + 6\text{CO}$ . This reacts with alumina (or dissociates) at higher temperatures (2100°, say), yielding aluminium, which may probably be dissolved in the carbide (otherwise it would distil away because its boiling point is about 1800°); on cooling, the aluminium separates out of the solution, which explains why aluminium and its carbide were found side by side in the product. T. E.

**Advances in the Domain of the Ceramic Industry.** WILHELM PUKALL (*Ber.*, 1910, 43, 2078—2106).—An account of the history of, and recent advance in, the domain of the ceramic industry. J. J. S.

**Manufacture of Cementation Steel. VII. Cementation based on the Specific Action of Carbon Monoxide.** FEDERICO GIOLITTI and G. TAVANTI (*Atti R. Accad. Sci. Torino*, 1910, 45, 539—563).—It is shown that fracture frequently takes place in steels along a boundary between two portions of different structure, due to segregation, the proportion of carbon being different on the opposite sides of the line of fracture. This segregation occurs during the slow cooling of the steel, and it is, therefore, desirable to find a process of cementation (case hardening) in which such segregation is avoided.

The steel is heated in a porcelain tube, the ends of which are packed with purified carbon, whilst a current of carbon dioxide is led slowly through the tube. The steel is then in contact with a mixture of carbon monoxide and dioxide in equilibrium with carbon at the given

temperature. The steel preserves its bright surface during the process of cementation. The carbon is in this way much more evenly distributed in the outer layers of the steel than when ethylene is used, and the brusque transition from high to low carbon steel in the outer zone does not occur.

C. H. D.

**Thorium Sulphate.** BARRE (*Compt. rend.*, 1910, 151, 231—234).

—Experiments have shown that aqueous solutions of thorium sulphate have a specific resistance and freezing point in good agreement with the laws of Bouy and Raoul. Similar cryoscopic and conductivity determinations have confirmed the existence of the double sulphate of potassium and thorium described in a previous communication (this vol., ii, 718).

W. O. W.

## Mineralogical Chemistry.

**Analyses of Seligmannite, Zinciferous Tennantite, and Fuchsite from Binn, Switzerland.** GEORGE T. PRIOR (*Min. Mag.*, 1910, I, 385—387).—The following analyses are given of minerals from the crystalline dolomite in the Lengenbach quarry. The rare mineral seligmannite, described by H. Baumhauer in 1901, has not previously been analysed; but from a consideration of the crystalline form it was predicted to be the sulpharsenite of copper and lead,  $\text{CuPbAsS}_3$ , isomorphous with bournonite ( $\text{CuPbSbS}_3$ ). This prediction is fully confirmed by the following analyses: I agrees closely with the above formula, while the material of II was perhaps not quite so pure:

	Pb.	Cu.	Ag.	Zn.	Fe.	As.	Sb.	S.	Total.	Sp. gr.
I.	46.34	13.09	0.11	0.27	0.06	16.88	0.64	21.73	99.12	5.44
II.	48.83	10.51	0.23	—	0.30	16.94	0.71	22.01	100.03	5.48
III.	—	42.03	1.24	7.76	0.62	19.30	—	28.08	99.53	4.61

Analysis III is of zinciferous tennantite ("binnite") with the form of cubes, the faces of which are deeply striated parallel to one diagonal, this is, parallel to the edges of intersection with small tetrahedral faces.

Clear, green crystals of muscovite (fuchsite) gave:

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Cr}_2\text{O}_3$ .	FeO.	CaO.	MgO.	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{Li}_2\text{O}$ .	Loss on ignition.	Total.
	47.24	31.86	0.87	0.56	0.58	2.91	10.72	0.16	0.14	5.37	100.41

L. J. S.

**Minerals Formed by the Combustion of Pyritous Shales in Midlothian.** S. JAMES SHAND (*Min. Mag.*, 1910, 15, 403—406).—

By the spontaneous combustion of a heap of shaly refuse at the Emily coal pit, Arncliffe, the following minerals have been formed: Native sulphur, as powdery encrustations and as minute crystals. Sal-

ammoniac, as fibrous crusts and small rhombic-dodecahedra. Tschermigite (?) (ammonia-alum) was detected amongst the material by qualitative tests. Mascagnite (ammonium sulphate), as fibrous and mealy encrustations. Halotrichite (?), as white to yellow, porous masses cementing fragments of cinder and burnt shale. When taken from the hot refuse heap this had a fused appearance, but it soon deliquesced on exposure to air. It is suggested that the white portion of this material may, while still hot, have been anhydrous aluminium sulphate (which would represent a new mineral species). Analysis of the portion soluble in water gave:

	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{SO}_3$
	20.44	10.57	1.08	67.91
corresponding with				
	$\text{Al}_2(\text{SO}_4)_3$	$\text{Fe}_2(\text{SO}_4)_3$	$\text{CaSO}_4$	$\text{H}_2\text{SO}_4$
	68.13	26.28	2.62	2.97

L. J. S.

**Rivotite.** ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1910, 33, 190—192).—This name was applied by Ducloux, in 1874, to a compact, yellowish-green material from Spain; his analysis showed:  $\text{Sn}_2\text{O}_3$ , 42.00;  $\text{Ag}_2\text{O}$ , 1.18;  $\text{CuO}$ , 39.50;  $\text{CO}_2$ , 21.00 = 103.68. A very similar material is now being worked as an ore at Irazain, near Sentein, dep. Ariège, France, where it forms head-like masses in dolomites of Devonian age. This is olive-green or blackish-green with a dull, uneven fracture, and it sometimes encloses specks of tetrahedrite and strings of malachite and chersylite. To all appearance the material is homogeneous, but thin sections under the microscope show around grains of tetrahedrite concentric layers of a golden-yellow isotropic material and of a greenish-yellow birefringent material. The latter is dissolved out by ammonia or by acetic acid, and consists of malachite, whilst the former is a hydrated oxide of antimony soluble in hydrochloric acid. The original Spanish material presents the same microscopical characters, and was proved to contain water. Rivotite is therefore an intimate mixture of malachite and stibiconite resulting from the alteration of tetrahedrite.

L. J. S.

**Datolite** from the Lizard District, Cornwall. W. F. P. McLINTOCK (*Min. Mag.*, 1910, 15, 407—414).—A new occurrence of crystallised datolite (a mineral only once before recorded in England) has been discovered at the junction of a serpentine and hornblende-schist at Park Bean Cove in the parish of Mullion. The associated minerals in the crystal-lined cavities are calcite, rarely natrolite, and specks of copper-pyrites. Massive datolite and the botryolite variety are also present. A detailed crystallographic description is given, and the optical constants determined. The following analysis agrees closely with the usual formula:  $\text{HCaBSiO}_5$ .

$\text{SiO}_2$	$\text{CaO}$	$(\text{Fe}, \text{Al})_2\text{O}_3$	$\text{B}_2\text{O}_3$	$\text{H}_2\text{O}$	Total.	Sp. gr.
37.45	34.67	0.57	21.87	5.67	100.23	3.061

L. J. S.

**A Soda-sanidine from Mitrowitz.** FRANZ ANGEL (*Jahrb. Min. Beil. Bd.*, 1910, 30, 254—268).—The analysis of a soda-sanidine from Mitrowitz gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Total
62.04	21.60	2.29	0.95	0.53	6.73	4.92	99.06

corresponding with  $8\text{KAlSi}_3\text{O}_8, 9\text{NaAlSi}_3\text{O}_8$ .

Crystallographic investigations show that it is really an orthoclastic felspar with unusually abnormal optical orientation. It stands in the same relation to the soda orthoclases as does the normal sanidine to ordinary orthoclase.

T. S. P.

**A New Mineral from the Iron Mines near Segré (Maine-et-Loire).** ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1910, 33, 270—273).

—This mineral, which has previously been considered as hiotite, occurs in a vein, together with chalybite, quartz, and some galena, at the junction of beds of magnetite with an altered diorite in the Minguet mine. It forms confused aggregates of opaque, black or greenish-black plates, somewhat resembling stilpnomelane in appearance. In convergent polarised light a dislocated black cross is seen, the optical sign being negative. The very strong dichroism is black and opaque to clear yellow. Before the blowpipe the mineral fuses to a black magnetic enamel; and all the water is lost at a low red-heat. It is easily attacked by hydrochloric acid, leaving pearly scales of silica. Analysis by F. Pisani gave the following results, agreeing with the formula:  $17\text{SiO}_2, 4(\text{Fe}, \text{Al})_2\text{O}_3, 8(\text{Fe}, \text{Mg})\text{O}, \text{K}_2\text{O}, 8\text{H}_2\text{O}$ .

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O	Total	Sp. gr.
43.65	5.22	18.80	19.00	3.22	0.94	0.66	3.00	6.00	100.49	2.86

The mineral thus differs from the micas in the small amount of alumina and alkalis, and also in the water being expelled at a lower temperature. It approaches more nearly to stilpnomelane, from which, however, it differs in containing alkalis and much ferric iron. Since the chlorites are characterised by the absence of alkalis, the name *minguetite* is proposed for this mineral, which in composition is intermediate between the iron-mica lepidomelane and the iron-chlorite stilpnomelane.

L. J. S.

**Structure and Composition of the Chandakapur Meteoric Stone.** HERBERT L. BOWMAN and HERBERT EDMUND CLARKE (*Min. Mag.*, 1910, 15, 350—376).—A description is given of one of three meteoric stones which fell near Chandakapur, in the Berar valley, India, on June 6, 1888. The structure is chondritic. Full details are given of the methods of analysis; briefly these are: (i) A preliminary separation of the magnetic material from the dry powder by means of a magnet, and the extraction of the metallic constituents from the two portions so obtained, by the prolonged action of a solution containing mercuric chloride, in an atmosphere freed from oxygen. (ii) The reduction of rust, magnetite, sulphides, and phosphides to the metallic state by ignition in hydrogen, and extraction of the resulting metals with mercuric solution. (iii) The separation of the silicates into two

# ABSTRACT OF CHEMICAL PAPERS.

...with Hydrochloric acid under conditions favour-  
...olivine but not of pyroxene or felspar. (iv) The  
...of the resulting fractions and the estimation of alkalis and of  
...phosphorus by the usual analytical methods.  
...combined results give the following bulk composition of the  
...ite:

Metallic.			Combined as schreibersite and troilite.			Rust and magnetite.			Chromite.
Fe.	Ni(Co).	Cu.	Fe.	Ni(Co).	P.	S.			
5.25	0.55	trace	3.73	0.31	0.16	1.79	0.3		0.51
SiO <sub>2</sub> .	MgO.	FeO.	CaO.	NiO.	Al <sub>2</sub> O <sub>3</sub> .	Na <sub>2</sub> O.	K <sub>2</sub> O.	Total.	
38.02	21.31	19.81	2.42	0.07	4.17	1.26	0.29	99.35	

The corresponding mineralogical composition is:

Metallic alloys.	Troilite.	Schreibersite.	Chromite.	Rust and magnetite.	Olivine (and some "glass").	Pyroxene (and felspar).
5.80	4.92	1.06	0.51	0.30	53.47	33.89

L. J. S.

## Physiological Chemistry.

What Influence does the Exact Estimation of the Tension of Water Vapour Exert on the Results Obtained in the Respiration Experiments in the Regnault Reiset Apparatus as Modified by Zuntz and Oppenheimer. HANS MÜRSCHHAUSER (*Biochem. Zeitsch.*, 1910, 27, 147—169).—In calculating the volume of oxygen and nitrogen in the apparatus at the beginning and end of the experiment, it has been generally assumed that the air is saturated with water-vapour. This the author shows is not the case, and he calculates the possible errors due to the neglect of this fact. He corrects for the error by estimating the degree of saturation of air in the apparatus by means of a hygrometer, and gives experimental examples to show how by this means the error can be reduced, illustrating his points both by combustion of alcohol in the apparatus and by actual respiration experiments on infants. S. B. S.

Periodic Breathing at High Altitudes. The Estimation of Total Oxygen Capacity and Blood-volume at Different Altitudes by the Carbon Monoxide Method. C. GORDON DOUGLAS (*J. Physiol.*, 1910, 40, 454—471, 472—479).—Increase of altitude increases the duration of the periodic breathing which follows apnoea produced by forced breathing; indeed, Cheyne-Stokes breathing may at a sufficient altitude become permanent. The cause is deficiency

of oxygen. Circulatory changes may, however, under certain conditions, produce a psychic influence is negligible.

Determinations of the total oxygen capacity in the same individual by the carbon monoxide method give variable results of the mean value. At high altitudes partial saturation of the blood with carbon monoxide renders him, comparatively speaking, incapable to make colorimetric observations. Fallacy may also arise from the experiment lasting too short a time for thorough admixture of the whole blood and the gas to occur. W. D. H.

**The Influence of Oxygen Pressure on the Gaseous Exchange of Certain Sea Animals.** MARTIN HENZE (*Biochem. Zeitsch.*, 1910, 26, 255—278).—The animals were kept in closed vessels at constant temperature in sea-water with varying contents. The oxygen was estimated in the water by Winkler's method before and after the experiments. There was generally found to be a certain maximum oxygen concentration, beyond which the oxygen consumption did not increase. The oxygen consumption in the case of fertilised eggs was independent of the oxygen content of the water. S. B. S.

**Respiratory Quotients after Exclusion of the Abdominal Organs.** ORRO FORGES (*Biochem. Zeitsch.*, 1910, 27, 131—142).—It was found that in rabbits with artificial respiration, in which the abdominal organs had, by means of ligatures, been excluded from the circulation, the respiratory quotient was higher than in control animals treated in the same way, but in which circulation through the abdominal organs remained intact. The author interprets the result as indicating that only carbohydrates are utilised under the former conditions, as the fats and proteins can only be utilised when the liver is intact; these substances probably undergo such changes in that organ that carbohydrates can be formed from them. S. B. S.

**The Respiratory Quotients of Dogs with Pancreatic Diabetes when the Abdominal Organs are Excluded from the System.** ORRO FORGES and H. SALOMON (*Biochem. Zeitsch.*, 1910, 27, 143—146).—As the respiratory quotient is higher in diabetic animals with abdominal organs excluded from the circulation than in similar control animals with circulation intact, the conclusion is drawn that in diabetes the capacity of the organism for burning sugar remains intact. S. B. S.

**The Distribution of Reducing Substances in Rabbit's Blood.** H. LYTTEKENS and J. SANDGREN (*Biochem. Zeitsch.*, 1910, 26, 382—390).—The reducing substances were estimated by Bang's method in serum, corpuscles, etc., both before and after submitting the protein-free liquids to fermentation. It was found that both serum and corpuscles contain reducing substances. In the corpuscles the quantity is from 0.07 to 0.08, and in the serum 0.27% (calculated as dextrose). Sucrose appears to be absent. After bleeding, the reducing substances increase to 0.14% in the case of the corpuscles, and to 0.60% in the case of serum. After phloridzin poisoning, the content

in reducing substances is the same as in normal blood; and after adrenaline, about the same as in animals after blood-letting. A part of the sugar in circulating blood exists apparently in a form of combination. The whole of the sugar is in the serum (normal quantity, 0.22%). The remainder of the reducing substance is not sugar (conclusions from fermentation tests). S. B. S.

**Conjugation as Sulphonyl Derivatives.** ENUARDO FILIPPI (*Chem. Zentr.*, 1910, i, 1981; from *Arch. Farm. speriment.*, 1910, 9, 158—172).—Small quantities of phenol in blood can be detected by physical changes, such as conductivity, freezing-point depressions, surface-tension, etc. After injection of phenol, guaiacol, and thiozol (potassium guaiacolsulphonate), free phenols can be detected in the blood by these physical or chemical methods only for a short time, and in small quantities, even after addition of toxic doses. Even after one to two hours, the phenols circulate in the form of sulphuric acid esters. S. B. S.

**Relation of the Pancreas to Blood Diastases in Dogs.** H. OTTEN and T. C. GALLOWAY, JR. (*Amer. J. Physiol.*, 1910, 23, 347—353).—After extirpation of the pancreas, the diastases of the blood are either destroyed or eliminated in a short time. Later, they again appear, showing that the pancreas is not the sole seat of their origin, although it is probably an important one. The point is discussed whether the blood diastases are related to sugar metabolism or are waste products, or whether they are of two kinds: (1) those of pancreatic origin of no significance in metabolism, and (2) those from other organs (possibly the liver), which may play an important part in the destruction of glycogen. W. D. H.

**The Nature of the Antitrypsin Formation in the Organism.** A. BRAUNSTEIN and L. KEPINOFF (*Biochem. Zeitsch.*, 1910, 27, 170—173).—The authors contend that the increased formation of antitrypsin in blood-serum is due to cell degradation, and the setting free of the intracellular, proteolytic, or autolytic ferments. They show that the antitryptic action of the serum can be increased by the injection intraperitoneally of liver or carcinoma paste if the material is not previously heated. If it is heated before injection, no increased antitrypsin formation is observed. S. B. S.

**Quantity of Secretion in a Given Gastric Fluid.** JUSTUS WINTER (*Compt. rend.*, 1910, 151, 165—167).—A discussion of the influence of test meals on the concentration of the gastric fluid. W. O. W.

**Calcium Metabolism and its Relationship to Phosphoric Acid and Magnesium Metabolism.** MARTIN KOCHMANN (*Biochem. Zeitsch.*, 1910, 27, 85—86).—In an adult dog, it is impossible under normal conditions to determine a minimum of calcium necessary for maintenance of equilibrium, since the calcium balance is influenced by the amounts of ingested protein, fat, and probably also carbohydrate.

for by adding these to the original diet, a considerable quantity of calcium is eliminated by the organism. Calcium equilibrium can be reconstituted by the addition of calcium to the increased diet. For these reasons, the calcium equilibrium can be varied at will. Magnesium behaves in a similar way. Phosphoric acid metabolism is influenced by the amount of protein and calcium ingested. The peculiar behaviour of the lime is explained by assuming that the excess is rendered harmless by entering into combination with the harmful or unused metabolites, and thus eliminated from the body. S. B. S.

**The Influence of Long-continued Ingestion of Nucleic Acid on the Purine Metabolism and the Excretion of Allantoin in the Dog.** WAICHI HIROKAWA (*Biochem. Zeitsch.*, 1910, 23, 441—457).—A small dog could tolerate for three months 5 grams of sodium nucleate daily added to a mixed, but fairly uniform, diet without suffering any ill effects. The purine bases ingested in this form were excreted chiefly as allantoin, and only a small portion in the form of uric acid or purine bases, even on superimposition of lead poisoning. About 72—88% of the ingested purine bases appeared in the urine in the form of purine substances or allantoin. Every gram of the ingested bases corresponded with an increased output of 0.0519 gram of nitrogen in the urine in the form of purine substances or allantoin. With long-continued feeding, the amount of allantoin excreted decreased, whereas that of uric acid increased, until after ten weeks the amount of uric acid was about ten-fold that of the first week. Lead poisoning caused a still greater increase. At the beginning of the nucleic acid ingestion, the uric acid nitrogen was about 1% of the sum of the purine and allantoin nitrogen; it afterwards increased to 13% without any corresponding increase of the purine base nitrogen. During the ingestion of excess of purine bases, therefore, the organism loses its capacity of oxidising uric acid to allantoin. S. B. S.

**The Physiology of Winter Sleep.** FELIX REACH (*Biochem. Zeitsch.*, 1910, 23, 391—405).—Dormice lose during the first two months of their winter sleep on an average 0.26% of their body-weight daily, of which more than half is attributable to loss of fat. No glycogen was formed during winter sleep, in fact, a certain quantity was lost. Whilst the absolute quantity of this substance lost was small compared with the fat, the relative proportions of these two substances as compared with their total quantity stored in the animal body was about the same. During the sleep both the fat and glycogen accumulated in the liver. The quantitative composition of the fat did not alter very much during the winter sleep; those acids, however, with the molecule smaller than that of palmitic acid appeared to be destroyed first; the other fatty acids gave no evidence of change, nor could an increase of the hydroxy-acids be ascertained. S. B. S.

**Changes in the Fats of the Hen's Egg during Development.** ELIZABETH C. EAVES (*J. Physiol.*, 1910, 40, 451—453).—As the fat decreases in the yolk, that in the chicken increases; there is some loss



due to fat being used to furnish energy; the low respiratory quotient indicates utilisation of fat. During the first ten days of incubation the iodine value of the yolk fat falls from 70 to 64, and after this to 44; that of the chicken fat is at first low and rises later. The low value at first may be due to the presence of other substances (especially a brown substance, supposed to be glycerol and glycerol-phosphoric acid) in the fat. The increase later points to a desaturation of the absorbed fat. The theory of Leathes, that the formation of double linkings is the first step in the oxidation of fat, is supported. W. D. H.

**Inhibition of the Toxic Action of Hydroxyl Ions on the Eggs of the Sea-Urchin by means of Potassium Cyanide.** JACQUES LOEB (*Biochem. Zeitsch.*, 1910, 26, 279—288).—The author assumes that hydroxyl ions act toxically by accelerating oxidation. By withdrawal of oxygen, or the addition of potassium cyanide, this oxidative process can be inhibited. If either fertilised or unfertilised eggs of *Strongylocentrotus purpuratus* were placed in artificial sea-water (50 c.c. of 0.54% *m*-NaCl + 1.1 c.c. *m*/2-KCl) containing excess of alkali, and then transferred to normal sea-water and fertilised, they did not develop normally. In a control experiment in which potassium cyanide in addition to alkali was added, normal development proceeded. The author discusses the theory of the action of alkali on fertilised and unfertilised eggs. S. B. S.

**Inhibition of the Toxic Action of Hydroxyl Ions on the Unfertilised Egg of the Sea-Urchin by Withdrawal of Oxygen.** JACQUES LOEB (*Biochem. Zeitsch.*, 1910, 26, 289—292).—One set of eggs was kept in sodium chloride solution and alkali in the presence of a current of air, and the other was kept under similar conditions, but in presence of hydrogen. Those eggs kept under the former conditions were rapidly destroyed, whilst the others could be kept for some hours, and, after transference to sea-water and fertilisation, developed in the normal way. If kept for too long under these conditions, however, they could not be developed. (For theory, see preceding abstract.) S. B. S.

**The Distribution in the Organs of Ferments Capable of Splitting Asparagine.** OTTO VON FÜRNBERG and M. FRIEDMANN (*Biochem. Zeitsch.*, 1910, 26, 435—440).—A ferment capable of liberating ammonia from asparagine was found in all organs. The method of experiment was to determine the amount of ammonia set free by similar portions of organs incubated with and without asparagine. In the case of the mucous membrane of the small intestine, the amount of ammonia liberated was so great as to indicate the scission of this substance from the amino- as well as from the amido-group. S. B. S.

**Hemolysis in the Liver.** LEONARD FINDLAY (*J. Physiol.*, 1910, 40, 445—450).—The blood of the hepatic vein contains in the majority of experiments recorded more red corpuscles than that of the portal vein; this is probably due to lymph formation and consequent

concentration of the blood. The hæmoglobin roughly runs a parallel course. No free hæmoglobin occurs in hepatic blood. The experiments, therefore, lend no support to the view that hæmolysis occurs in the liver. The animals experimented with were cats.

W. D. H.

**The Inhibition of Acetoacetic Acid Formation in the Liver.** GUSTAV EMBDEN and JOSEPH WIRTH (*Biochem. Zeitsch.*, 1910, 27, 1—19).—The authors, by perfusion experiments, have already shown that certain substances give rise to acetone substances in the liver (leucine, isoleucine, tyrosine, phenylalanine, etc.). They now show that other substances, when added to these in the blood-mixture used for perfusion, inhibit the increased formation of acetone substances. Amongst such substances are *n*-valeric acid, amino-*n*-hexoic acid, and, to a less degree, isohexoic acid. The inhibitory character depends apparently on the combustibility of these substances in the liver; when these are present, the substances giving rise to acetone substances are acted on so slowly, the acetoacetic acid, etc., formed so slowly, that they are destroyed without accumulating. A high content of glycogen in the liver also inhibits the acetone formation from isovaleric acid, although dextrose is without effect on this factor. From this fact, the conclusion is drawn that stored glycogen is more readily burnt than dextrose. *dl*-Alanine and *dl*-lactic acid are also without effect on acetoacetic acid formation; no definite conclusions could be drawn as to the action of glycerol.

S. B. S.

**Acetoacetic Acid Formation in the Liver of a Diabetic Dog.** II. WALTER GRIESBACH (*Biochem. Zeitsch.*, 1910, 27, 34—37).—It has been shown by Embden and Wirth (preceding abstract) that the addition of *n*-valeric acid inhibits the formation of acetone when substances which are normally acetone formers are perfused through the liver. In dogs which have been rendered glycosuric either by pancreas extirpation or phloridzin, this inhibition by *n*-valeric acid does not take place. The explanation of this fact which is considered most probable by the author is, that the livers of animals which have been rendered diabetic have so much fat stored up intracellularly, which is so readily combustible with formation of acetone substances, that the addition of other added combustible substances, such as *n*-valeric acid, exerts no influence on the formation of acetone substances.

S. B. S.

**The Degradation of isoLeucine in the Liver.** JOSEPH WIRTH (*Biochem. Zeitsch.*, 1910, 27, 20—26).—When isoleucine or  $\alpha$ -methylbutyric acid, which is assumed to be an intermediary degradation product of the former, are perfused through the liver there is sometimes an increased formation of acetone substances, and at other times not. There are various ways by which degradation can take place, as either the methyl or the ethyl group can be oxidised. In the former case only is an acetone-forming substance formed. That the ethyl group can also be destroyed is shown by the experiments with  $\beta$ -methylvaleric acid, which on perfusion gives rise to increased formation of

acetone substances, the formation of which can only arise by the destruction of the ethyl group. Ethylbutyric acid also gives rise to variable results.

S. B. S.

**Degradation of Leucine in the Liver.** FRITZ SACHS (*Biochem. Zeitsch.*, 1910, 27, 27—33).—It has been shown that amino-acids behave in the liver with regard to the formation of acetone substances like the amino-free acid containing one carbon atom less, and not like those with the same number of carbon atoms. From this it appears as if the amino-acids are degraded by deamidation and oxidation of the terminal carbon atom. If oxidation takes place before deamidation, the possible intermediate product in the degradation of leucine is isosamylamine, from which by deamidation, isosamyl alcohol, isovaleraldehyde, and isovaleric acid can be produced. If deamidation precedes oxidation, the immediate products would be isobutylhydroxyacetic (leucic) acid, from which by deamidation and scission of carboxyl group, isosamyl alcohol, etc., would be produced. To gain an insight into the method of degradation of leucine, the behaviour of these various substances with regard to acetone formation in the liver was investigated. All the above substances were found to be powerful acetone-formers, with the exception of isosamyl alcohol, which in larger doses was toxic to the liver. No definite conclusions could be drawn from these experiments, therefore, as to the method of leucine degradation. No marked difference was found between the behaviour of *L*-leucic acid and *D*-leucic acid, which is in marked contrast to what has been found in the case of *L*-leucine and *D*-leucine.

S. B. S.

**Liver Functions (Deamidation, Reduction, and Carbon Dioxide Cleavage in the Artificially Perfused Liver).** OTTO NEUBAUER and HANS FISCHER (*Zeitsch. physiol. Chem.*, 1910, 67, 230—240).—If the surviving liver of the dog is perfused with a mixture of dog's blood and Ringer's solution, and phenylaminoacetic acid added, the *D*-component is so altered that the *L*-acid remains in excess. The deamidised product of the amino-acid is the corresponding ketonic acid (phenylglyoxylic acid). Secondly, this is reduced to *L*-mandelic acid, and, in part, changed into benzoic acid. Whether other tissues behave in a similar way has yet to be tested, but the evidence available is in favour of the liver being the principal seat of such changes.

W. D. H.

**Tyrosine Catabolism in the Artificially Perfused Liver.** OTTO NEUBAUER and WALTER GROSS (*Zeitsch. physiol. Chem.*, 1910, 67, 219—229).—The method adopted for perfusion is described with full detail; by practice the perfusion with dog's blood diluted with Ringer's solution can be commenced ten minutes after the excision of the liver; the amount of acetone in the outflowing fluid is increased, as Embden showed; the addition of *p*-hydroxyphenylpyruvic acid leads to an enormous increase of acetone similar to that produced by the addition of a corresponding quantity of tyrosine. The addition of *p*-hydroxyphenyl- $\alpha$ -lactic acid has no such effect. These results, together with those obtained in metabolic experiments on alcaptonuric patients

support the hypothesis that the ketonic acid,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , is the normal product of intermediate tyrosine metabolism, and not the alcohol acid,  $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ . W. D. H.

**The Constituents of Animal Organs Soluble in Ethyl Acetate, and their Behaviour During Autolysis. I. Does the Liver Contain Cholesterol Esters?** KENRO KONDO (*Biochem. Zeitsch.*, 1910, 26, 238—242).—An alcoholic extract of livers was made, from which the alcohol was evaporated off. An extract with ethyl acetate was made of the residue, and the "acetyl number" of the substances extracted was determined both before and after hydrolysis with alcoholic potassium hydroxide. From the fact that this number is larger after hydrolysis than before, the conclusion was drawn that cholesterol esters were present, and that, in fact, about 39% of the total cholesterol in the organ existed in the form of esters. The same results were obtained if the experiment was carried out after precipitation of the free fatty acids in the ethyl acetate extract by methyl-alcoholic barium hydroxide before determination of the acetyl numbers. The results are not due, therefore, to water-insoluble fatty acids. These results are not in accordance with those previously obtained by Nakada, working with a somewhat different method. S. B. S.

**The Constituents of Animal Organs Soluble in Ethyl Acetate, and their Behaviour during Autolysis. II. Does the Liver contain an Enzyme Capable of Splitting Cholesterol Esters?** KENAO KONDO (*Biochem. Zeitsch.*, 1910, 26, 243—251).—An emulsion of oleic acid, olive oil, and cholesteryl oleate showed, on incubation with unboiled (but not with boiled) liver extracts, a greater increase in the acetyl number than was shown if the extract alone was incubated. An increase in the acetyl number also took place when an oleic acid emulsion alone was treated with liver extracts. The results do not show conclusively whether an enzyme capable of splitting cholesterol esters was present, as they can be taken to indicate that oxidation of oleic acid to form substances with a larger number of hydroxyl groups can also have taken place. S. B. S.

**The Constituents of Animal Organs Soluble in Ethyl Acetate, and their Behaviour during Autolysis. III. The Formation of Hydroxy-Fatty Acids during Autolysis of the Liver.** KENRO KONDO (*Biochem. Zeitsch.*, 1910, 26, 252—254).—The acids obtained by precipitation of the ethyl acetate extracts (see preceding abstracts) by methyl-alcoholic barium hydroxide were added to the fatty acids obtained by hydrolysis from that part of the alcoholic extract of the liver which was not soluble in ethyl acetate. The acetyl number of the acids thus obtained was determined in equivalent portions of the liver extract both before and after autolysis. The increase in the acetyl number after autolysis indicated the formation of fatty acids during this process. S. B. S.

**The Importance of the Skin as a Dépôt of Chlorine.** J. H. PADTBERG (*Arch. exp. Path. Pharm.*, 1910, 63, 60—79).—On food either rich or poor in chlorides, the skin, blood, kidneys, and lungs contain

the highest, and the muscles the lowest, percentage of chlorine. On food rich in chlorides, the chlorine in the dog rises on the average 0.17%; on food poor in chlorides, it falls 0.137%; by intravenous injection of hypertonic salt solution, it rises 0.2%. On chlorine-poor food, the skin contains about one-quarter of the total chlorine in the body; on chlorine-rich food, this rises to one-third. After intravenous injection, the rise in chlorides is greatest in the skin; the lungs, intestine, blood, and kidneys follow in the order named. W. D. H.

**Phosphorus in Beef.** II. C. K. FRANCIS and PERRY F. TROWBRIDGE (*J. Biol. Chem.*, 1910, 3, 81—94. Compare this vol., ii, 731).—A large number of analyses of the different organs and cuts in various steers and cows are given. In young animals the results are fairly uniform, but this is not so in mature animals. The largest amount of phosphorus is found in the circulatory and nervous systems. In thin animals the results are usually lower. Further generalisation does not appear at present possible. W. D. H.

**The Glycogen Content in Tunicates; the Influence of Iron on the Estimation of Glycogen.** EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1910, 27, 53—60).—In tunicates (ascidea), in addition to cellulose, another polysaccharide (glycogen) is present in considerable quantities (not less than 26% of the dry weight of the organs). A diastatic ferment is also present, which is capable of acting at relatively low temperatures. In the course of the investigations it was found that an error existed in Pflüger's method for the estimation of glycogen, due to the presence of iron, which, in the form of hydroxide, is capable of absorbing considerable quantities of this polysaccharide. For this reason, after the tissues have been treated with alkali, the insoluble portion should also be examined, as it contains glycogen absorbed by the iron. This portion should be dissolved in hydrochloric acid, and the glycogen in the solution thus obtained determined. By neglecting this operation, an error of as much as 50% can be made in the glycogen determinations in certain cases. S. B. S.

**The Secretion of Cholesterol in Human Bile.** BACMEISTER (*Biochem. Zeitsch.*, 1910, 23, 223—230).—The amount of cholesterol secreted in four cases of human biliary fistula was investigated, the alcohol being estimated by the digitonin method of Windaus. The output altered greatly from day to day; the averages in the four cases varied between 0.11 and 0.23 gram daily. It was, however, appreciably lower immediately after the operation. S. B. S.

**The Alleged Occurrence of Trimethylamine in Urine.** C. C. ERDMANN (*J. Biol. Chem.*, 1910, 3, 57—60).—The volatile character of trimethylamine suggested that Folin's air current method which he uses for ammonia estimations might be employed. The test employed was the characteristic odour which Kaufmann states can be detected in dilutions as low as 1 in two millions. No trimethylamine could be detected in ten normal urines. It can be obtained from stale urine, or from any urine which has been subjected to Kjeldahl digestion. W. D. H.

**The Presence and Detection of Allantoin in Human Urine.** KARL ASCHER (*Biochem. Zeitsch.*, 1910, 26, 370—381).—The allantoin was obtained in crystalline form after precipitation by Wiechowski's reagent (mercuric acetate in sodium acetate solution), which was added after freeing the urine from various constituents by phosphotungstic acid and silver nitrate, and other treatment. In the case of a normal individual, 8 mg. of allantoin were recovered for one day's output of urine; in the case of a starving man, 1 mg. was obtained, and in a case of leucæmia, 5.6 mg. Allantoin was absent in a case of pernicious anemia, and its presence was doubtful in a case of Addison's disease. Allantoin is readily adsorbed by animal charcoal under certain conditions to the extent of more than 90%. The author finds that the naphtharesorcin test is not applicable, as under certain conditions colours can be obtained from the reagent itself in blank tests; neither is the peptone-sulphuric acid reagent applicable to urine.

S. B. S.

**The Occurrence of Creatine in Diabetic Urine.** R. A. KRAUSE and WILHELM CRAMER (*Proc. physiol. Soc.*, 1910, lxi—lxii; *J. Physiol.*, 40).—In typical diabetes mellitus, and in phloridzin glycosuria (in dogs), creatine is regularly found in the urine. It was also found in eight cases of pregnancy at the seventh or eighth month. Creatine occurs in all conditions that may lead to acidosis or to muscular atrophy. Creatine may appear before acidosis sets in, as in the cases of diabetes examined.

W. D. H.

**Formation of Sugar from Fat (in Phloridzin Diabetes).** FELIX LOMMEL (*Arch. exp. Path. Pharm.*, 1910, 63, 1—9).—It was thought that some light might be thrown on this vexed question by the administration of alcohol to dogs rendered diabetic with phloridzin. If sugar originates from fat, the removal of fat by alcohol would lessen the glycosuria, or cause some change in the dextrose: nitrogen ratio. The experiments gave varying and therefore disappointing results.

W. D. H.

**Alleged Anæsthetic Properties of Magnesium Salts.** CHARLES C. GUTHRIE and A. H. RYAN (*Amer. J. Physiol.*, 1910, 26, 329—346).—The authors do not agree with Meltzer and Auer that magnesium sulphate is very toxic, and that it has specific anæsthetic effect. The immobility after large doses is due rather to the effect on the neuro-muscular apparatus; if this produces, as it generally does, more or less asphyxia, loss of sensation is due to the asphyxia, and its amount will depend on the degree of asphyxiation.

W. D. H.

**Narcotics and Local Anæsthetics. II.** OSCAR GROS (*Arch. exp. Path. Pharm.*, 1910, 63, 80—106. Compare this vol., ii, 529).—The theory of narcosis of Hans Meyer and Newton applies to local anæsthetics; the base of local anæsthetics act more strongly than their salts. The anæsthetic potential of the salt depends on that of the base, and the degree of hydrolytic dissociation; that of novocaine

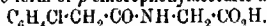
hydrogen carbonate is five times greater than that of the chloride. The bases of all the local anaesthetics investigated are about equal in strength, and affect sensory more readily than motor nerves. Eucaine and stovaine have the strongest, and novocaine the weakest, affinity for protein.

W. D. H.

**Action of Praseodymium, Didymium, and Erbium on the Frog's Heart.** GEORGE R. MINES (*Proc. physiol. Soc.*, 1910, lxxiii; *J. Physiol.*, 40).—The chlorides of the elements mentioned act in the same way as other rare earths. Neutral Ringer's solution containing 0.00001 mol. per litre stops the ventricle in a few minutes. Washing out with neutral Ringer's solution causes slow and imperfect recovery. The addition of a little alkali renders it prompt and complete. The fact that didymium and praseodymium tested alternately on the same heart show the same activity renders it probable that neodymium, the other constituent of didymium, has the same action as praseodymium.

W. D. H.

**The Degradation of Carboxylic Acids in the Animal Body.**  
**IX. The Behaviour of *p*-Chlorophenylalanine, *p*-Chlorophenylpyruvic Acid, and *p*-Chlorophenyl-lactic Acid in the Animal Body.** ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1910, 27, 97—112. Compare Abstr., 1908, ii, 719).—In the conversion of tyrosine into homogentisic acid in the organism, it has been assumed that a quinol derivative is formed as an intermediate product; this can only happen when an  $\alpha$ -hydroxyl group exists, or can be introduced into the para-position of the other substituting group. For this reason it was of interest to investigate the behaviour of those substances in which the para-position is already substituted by another group. These investigations should also throw some light on the method of degradation of the nitrogenous side-chain. The substances investigated with this object were *p*-chlorophenylalanine and *p*-chlorophenylpyruvic acid, both of which were excreted with glycine in the form of *p*-chlorophenylacetic acid,



The corresponding hydroxy-acid, *p*-chlorophenyl-lactic acid, was not excreted in this form, and the results indicate that amino-acids are broken down in the body with deamidisation into an acid with one carbon atom less, and that the corresponding  $\alpha$ -hydroxy-acids are not formed as intermediate products.

*p*-Chlorophenylalanine was prepared by condensing *p*-chlorobenzaldehyde with hippuric acid to form the lactimide of *p*-chloro- $\alpha$ -benzoylaminocinnamic acid,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5 \\ \text{CO} \end{smallmatrix}$  (m. p. 195°), which

on hydrolysis yielded *p*-chloro- $\alpha$ -benzoylaminocinnamic acid (m. p. 216°); this was reduced by sodium amalgam to benzoyl-*p*-chlorophenylalanine (m. p. 171—172°), which on treatment with hydrochloric acid yielded the hydrochloride of *p*-chlorophenylalanine. From this the free amino-acid (m. p. 243—244°) was obtained.

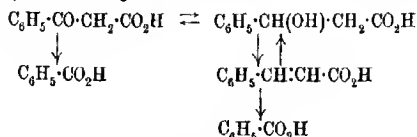
*p*-Chlorophenyl-lactic acid (m. p. 85—87°) was obtained from the above by the action of nitrous acid.

*p*-Chlorophenylpyruvic acid (m. p. 191°, decomp.) was obtained by the action of sodium hydroxide on *p*-chloro- $\alpha$ -benzoylamino-cinnamic acid.

*p*-Chlorophenylaceturic acid (m. p. 165°) was synthesised by the action of *p*-chlorophenylacetyl chloride (b. p. 120°/14 mm.) on glycine in presence of sodium hydroxide. S. B. S.

**The Degradation of Carboxylic Acids in the Animal Body.**  
**X. The Behaviour of  $\alpha\beta$ -Dihydroxy-acids in the Animal Body.** ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1910, 27, 113—118).—As both saturated and unsaturated acids yield the same products in the animal body, and as  $\beta$ -ketonic acids are supposed in both cases to be intermediate products, experiments were carried out with  $\alpha\beta$ -dihydroxy-acids to determine whether such acids were also intermediate products in the degradation of acids, and whether they also yield keto-acids, and are formed as the first stage in the degradation of the unsaturated acids. Perfusion experiments with  $\alpha\beta$ -dihydroxybutyric acid yielded no acetoacetic acid on perfusion, neither did phenylglyceric acid after ingestion yield acetophenone (or benzoylacetic acid). These results indicate that the dihydroxy-acids are not formed as intermediate metabolism products, and that probably, by addition of water at the double bond,  $\beta$ -hydroxy-acids are first formed, which oxidise to keto-acids. S. B. S.

**The Degradation of Carboxylic Acids in the Animal Body.**  
**XI. The Behaviour of Benzoylacetic Acid in the Animal Body.** ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1910, 27, 119—130).—In view of the conceptions advanced by Knoop and by Dakin as to the formation of  $\beta$ -hydroxy-acids as intermediate products in the degradation of acids in the animal body, and in view also of the fact that phenylpropionic acid entirely disappears after administration to animals, whereas the supposed intermediate product,  $\beta$ -hydroxyphenylpropionic acid, does not, experiments were carried out with the other possible intermediate product, namely, benzoylacetic acid. The following products were obtained in the urine when this substance was administered subcutaneously to dogs in doses of 0.35 gram per kilo. of body-weight: *l*- $\beta$ -hydroxyphenylpropionic acid, acetophenone, cinnamoylglycine, and hippuric acid. The author represents the changes by the following scheme:



From these results, and from those of other authors, it would appear that certain of the changes are reversible. S. B. S.

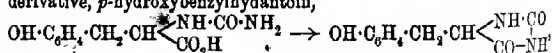
**Mode of Oxidation of Phenyl Derivatives of Fatty Acids in the Animal Organism. A Correction.** HENRY D. DAKIN (*J. Biol. Chem.*, 1910, 8, 35—39).—The substance previously in-



investigated (Abstr., 1909, ii, 635), and supposed to be phenyl- $\beta$ -alanine, turns out, as Posner showed, to be the amide of  $\beta$ -hydroxyphenylpropionic acid. Pure phenyl- $\beta$ -alanine was prepared by Posner's method, and given to dogs and cats either by the mouth or subcutaneously. The urine contains much of the unchanged acid; on concentration on the water-bath it reacts with carbamide to form  $\beta$ -carbamino-phenylpropionic acid, and this by the subsequent action of acids in the course of the analysis may be converted into the corresponding anhydride, phenyldihydrouracil. No indications of the formation of  $\beta$ -hydroxyphenylpropionic acid, acetophenone, or hippuric acid were found, so contrasting with the corresponding hydroxy- and ketonic acids, both of which are converted into hippuric acid. W. D. H.

**Mode of Decomposition of Tyrosine and of Related Substances in the Animal Body.** HENRY D. DAKIN (*J. Biol. Chem.*, 1910, 8, 11—24).—The experiments failed to demonstrate in normal animals the type of change necessary for the conversion of tyrosine or phenylalanine into homogentisic acid. The inference that the latter acid is not a normal product of catabolism is, however, still inconclusive. Jaffé found muconic acid in the urine of dogs after dosage with benzene; this suggests that the oxidation of the aromatic nucleus in phenylalanine and tyrosine may not necessarily be preceded by the introduction of hydroxyl groups into the ring. The frequent occurrence of the  $\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$  grouping in amino acids, which undergo complete decomposition in the body, is significant. The group readily undergoes condensation with other amino-acid groupings in the tissues, and this may be a necessary preliminary to the oxidation of aromatic nuclei. The fact that phenylaminobutyric acid undergoes easy oxidation in the body and in alcaptonuria is not converted into an alcapton acid, harmonises with this view, as also do certain other facts which are quoted. W. D. H.

**Fate of Inactive Tyrosine in the Animal Body, together with some Observations on the Detection of Tyrosins and its Derivatives in the Urine. The Synthesis and Probable Mode of Formation of Blendermann's *p*-Hydroxybenzylhydantoin.** HENRY D. DAKIN (*J. Biol. Chem.*, 1910, 8, 25—33).—Inactive tyrosine administered to cats undergoes selective decomposition, so that the tyrosine of the urine contains more of the dextro- than of the naturally-occurring lævo-variety. When neutral or alkaline urine which contains tyrosine is evaporated, the tyrosine is largely converted with the corresponding uramino-acid. On subsequent treatment with acids, this readily loses water, giving the hydantoin derivative, *p*-hydroxybenzylhydantoin,



described by Blendermann in the urine of rabbits dosed with tyrosine. Blendermann's substance is no doubt the result of analytical procedure. It is important to avoid heating the urine unless it is acidified. No homogentisic or similar acid was found. W. D. H.

**Action of Nicotine and Curare on the Receptive Substance of the Frog's Rectus Abdominis Muscle. Antagonism by Curare of the Nicotine Stimulation of Nerve Cells.** JOHN N. LANGLEY (*Proc. physiol. Soc.*, 1910, lix—lx, lxii; *J. Physiol.*, 40).—Further experiments are described which support the view that curare combines with the receptive substance and can be displaced by nicotine. This antagonistic action is fundamentally the same on autonomic nerve cells and on striated muscle.

W. D. H.

**[Physiological] Action of Tetrahydropapaveroline.** P. P. LAIDLAW (*J. Physiol.*, 1910, 40, 480—491).—Tetrahydropapaveroline hydrochloride was first prepared by Pyman (*Trans.*, 1909, 95, 1610), during his study of the reduction products of papaverine. It causes a fall of blood pressure, although the heart rate is increased; the fall is due to vascular dilatation; the respiration rate is augmented, and the plain muscle of the bronchioles is completely relaxed; the same is true for the arteries and, to a less extent, for the intestine; the bladder and skeletal muscle are not affected.

W. D. H.

**[Physiological] Action of Kamala and its Constituents.** AUG. SEMPER (*Arch. exp. Path. Pharm.*, 1910, 63, 10—37).—This anthelmintic is toxic to frogs, tadpoles, and worms. The symptoms produced in frogs are similar to those resulting from different *Filix* substances; the same similarity is seen in its action on muscle and nerve. The action of rottlerin, a substance obtained from kamala, and the ethereal extract show the same action in smaller degree. In dogs, kamala and its products are not absorbed, unless their use is prolonged, and then local changes in the intestine and albuminuria occur.

W. D. H.

**Certain Bases which Occur in the Urine During Phosphorus Poisoning.** K. TAKEDA (*Pflüger's Archiv*, 1910, 133, 365—396).—On the hypothesis that oxidation is lessened in the body in phosphorus poisoning, the urine of five dogs poisoned with that substance was examined for abnormal bases. The urine contained a trace of protein, but no sugar, leucine, or tyrosine. In all, 65 litres of urine were collected. After acidification with sulphuric acid, phosphotungstic acid was added. By fractional treatment of this precipitate with silver nitrate and mercuric chloride, compounds of certain bases were obtained, in some cases in crystalline form. The identification of these bases was incomplete; one appears to be isomeric with crangonine ( $C_{13}H_{20}O_5N_2$ ), a base separated from crab extract by Kutscher and Ackermann, and another with Brieger's base,  $C_7H_{15}O_2N$ , prepared from putrefying material. These are toxic, acting mainly on the heart, and lowering arterial pressure. Other bases somewhat similar to histidine and pyrimidine bases were found, but not identified; one suspected to be butyrobetaine gave an intense odour of trimethylamine when destroyed.

W. D. H.

**Thyroidectomy and the Resistance of Rats to Morphine Poisoning.** W. H. OLDS, jun. (*Amer. J. Physiol.*, 1910, 26, 354—360).—Rats survive thyroidectomy without harm, provided the

recurrent laryngeal nerves are intact and the parathyroids not entirely removed. They show the same resistance to morphine poisoning as normal rats.

W. D. H.

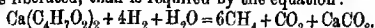
### Chemistry of Vegetable Physiology and Agriculture.

The Rôle of Methane in Organic Life. N. L. SÖHNGEN (*Rec. trav. chim.*, 1910, [ii], 14, 238—274. Compare Hoppe-Seyler, *Abstr.*, 1886, 577, 932).—The observations of Omelianski (*Abstr.*, 1902, ii, 468) relating to the fermentation of cellulose are confirmed.

The author has studied the fermentation of the calcium salts of fatty acids first observed by Hoppe-Seyler (*Abstr.*, 1887, 618, 1135; compare also Mazé, *Abstr.*, 1904, ii, 138; Pakes and Jollyman, *Proc.*, 1901, 17, 29). If a quantity of sewer or caecal mud (40 c.c.) is mixed with a solution (100 c.c.) containing 0.05% of dipotassium hydrogen phosphate, 0.05% of ammonium chloride, and 2% of a calcium salt of a fatty acid, and the mixture kept at 35°, a vigorous fermentation takes place. After several repetitions of the process, the residue becomes quite white, probably from the destruction of humus and formation of calcium carbonate. The active micro-organism is present only in the sediment, not in the supernatant liquor; the former, after repeated cultivation, is found to contain a bacterium and a sarcina, both of which ferment fatty acids. The bacterium takes the form of a small rod, 5—7  $\mu$  long and 0.3—0.5  $\mu$  wide; it is largely enveloped by the calcium carbonate, and predominates in cultures other than those of calcium acetate. The sarcina is rather larger, but less active, than the bacterium, and predominates in acetate cultures. Neither organism forms spores, both are killed at  $\pm 60^\circ$ , are active only in neutral liquids, and are stained by aniline dyes. The sarcina resists drying at 40°, whilst the bacterium is destroyed, and separation can be effected by these means. The activity of the bacterium is lessened by increasing the concentration of the salt of the fatty acid, and is inhibited when this amounts to 10%. This bacterium does not ferment cellulose. Experiments are described in which a culture residue, prepared as above, was treated with solutions of calcium butyrate and formate. The results of these show that the butyrate is fermented according to the equation:  $\text{Ca}(\text{C}_4\text{H}_7\text{O}_2)_2 + 3\text{H}_2\text{O} = 5\text{CH}_4 + 2\text{CO}_2 + \text{CaCO}_3$ , and the formate according to  $2\text{Ca}(\text{CHO}_2)_2 = \text{CH}_4 + \text{CO}_2 + 2\text{CaCO}_3$ . The calcium salts of other acids containing an even number of carbon atoms are decomposed by similar reactions. Acids containing an odd number of carbon atoms, except formic acid, are not attacked.

When the pure culture of Omelianski's methane-forming bacillus, obtained by repeated cultivation with pasteurisation of a dung-culture, is inoculated in a sterile solution of mineral salts containing filter paper and calcium carbonate, and placed in an atmosphere of hydrogen, the latter gradually disappears, whilst methane and carbon dioxide are evolved.

Similarly, if a solution of calcium butyrate in a hydrogen atmosphere is inoculated with the sediment of a culture of the acid-fermenting organism, the hydrogen is absorbed, whilst methane and carbon dioxide are liberated. More hydrogen, however, is absorbed, and less of the other gases liberated, than is required by the equation :



A similar discrepancy is observed in experiments with calcium formate. This discrepancy is explained by the observation that carbon dioxide (from the calcium hydrogen carbonate present in the culture) under the influence of the organism is reduced by hydrogen to methane. Thus a mixture of 1350 c.c. of hydrogen and 300 c.c. of carbon dioxide, confined at 35° under pressure in a vessel containing a solution of mineral salts and a culture of the acid-fermenting bacterium, diminished in eighteen days to 444 c.c., composed of 159 c.c. of hydrogen and 285 c.c. of methane, in accordance with the equation :  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ .

The paper ends with an account of work on the *Bacillus methanicus*, already published (Abstr., 1906, ii, 42). E. H.

Biochemistry of Micro-organisms. III. The Fermentation of Formic Acid by the *Bacillus phymonthiensis*. HARTWIG FRANZ and G. GREVE (*Zeitsch. physiol. Chem.*, 1910, 67, 251—296. Compare this vol., ii, 333).—Further details regarding the fermentation of formic acid are given in reference to varying conditions of temperature, etc. Two strains of the *B. phymonthiensis* (K. G. A. and Kräb), although morphologically so much alike, differ in their relative action in this direction. W. D. H.

A Chemically Characterised Hæmolytic of Bacterial Origin, Hydroxythiodimethylerythric Acid, the Hæmolytic of *Bacterium Putidum* (Lehmann and Neumann). LUDWIG BURKHARDT (*Arch. exp. Path. Pharm.*, 1910, 63, 107—118).—The substance produced by *B. putidum* which acts as a hæmolysin is a monobasic unsaturated acid, which was identified as *hydroxythiodimethylerythric acid*,  $\text{C}_{24}\text{H}_{46}\text{O}_8\text{S}$ , probably  $\text{OH}\cdot\text{C}_{22}\text{H}_{43}\text{Me}\cdot\text{CO}\cdot\text{SH}$ . Several of its salts were prepared ; on oxidation it yields dihydroxybehenic acid ; whether immunisation against it can be produced has not yet been attempted. W. D. H.

Oxidation of Acetaldehyde by Lower Vegetation. A. PENRIER (*Compt. rend.*, 1910, 151, 163—165).—A species of *Torula* was cultivated in a medium containing definite amounts of acetaldehyde, but free from other organic substances. Progressive disappearance of aldehyde was observed, but no products of incomplete oxidation were detected. Negative results were obtained in similar experiments with formaldehyde. The results confirm the theory that alcohol and aldehyde are two successive stages in the degradation of sugars by micro-organisms. W. O. W.

The Dependence of Plant Respiration on the Presence of Lipoids. WLADIMIR PALLADIN and E. STANEWITSCH (*Biochem. Zeitsch.*, 1910, 26, 351—369).—Wheat embryos were extracted with different organic solvents, and then soaked for a short time in water.

The amount of carbon dioxide evolved during definite intervals was then estimated. It was found that those solvents which extracted the most lipid substance and phosphorus depressed most the respiration energy. In order to obtain killed plants with the most active ferments, it is needful to employ substances in which the lipoids are least soluble. Toluene vapour exerts an injurious effect on the carbon dioxide excretion of plants; the toxicity varies with the nature of the solvent which had been employed for the extraction of the seedlings.

S. B. S.

**Vegetable Assimilation and Respiration. VI. Some Experiments on Assimilation in the Open Air.** D. THODAY (*Proc. Roy. Soc.*, 1910, B, 82, 421—450).—Notwithstanding the low concentration of carbon dioxide in the air, high rates of assimilation occur. Leaves of *Helianthus annuus* showed an average net rate of increase of 17 mg. per hour in their dry weight per square dm., a result agreeing closely with that obtained by Sachs (16.5 mg.). It is probable that when the stomata allow sufficient carbon dioxide for this assimilation to diffuse into the leaf, the internal leaf-temperature will be the limiting factor unless it exceeds 23—25°.

The high results obtained with *H. annuus* indicate that the waste of available energy on a bright day has been over-estimated. On sunny days the waste is probably about 70%, and sometimes less.

The low results obtained by Brown and Escombe (5.5 mg.) are attributed partly to the unnaturally high temperatures in the glass leaf-cases employed; and it is probable that the stomata were not fully open. It is suggested that the failure of oven very bright diffused light fully to open the stomata of *H. annuus* depends, not on the photosynthetic value of the radiation, but on the relative poverty in heat rays.

Whilst attached leaves have to absorb water from the stem against a negative pressure, the resistance has no longer to be overcome when the leaves are detached, and such leaves may be expected to open their stomata more widely than similar leaves still on the plant.

N. H. J. M.

**The Behaviour of Nuclein Bases in the Dark in Plants.** ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1910, 67, 241—250).—Although the nuclein bases in plants are so similar to those in animals, uric acid has never been found in the vegetable kingdom. In the dark, deamidation takes place, and xanthine and hypoxanthine increase at first, whilst adonine and guanino disappear. Later, the two former bases also diminish. There is no trace of uric acid found. Whether allantoin is formed has still to be discovered. W. D. H.

**Chemical Examination of the Oil from the Seeds of *Bursaria spinosa* (Blackthorn).** EDWARD GRIFFITHS (*J. Roy. Soc., New South Wales*, 1909, 43, 399—405).—The seeds of *Bursaria spinosa* yield by extraction with light petroleum about 17% of a yellow, transparent oil having the following constants: saponification number, 169.47; iodine number (Hübl), 86.1; D<sub>4</sub><sup>20</sup> 0.8567; acid

number, 1-26; n<sub>D</sub><sup>20</sup> 1-4681. The oil appears to consist mainly of olein with small quantities of stearin. Amongst the unsaponifiable constituents of the oil is a phytosterol and a wax-like substance, m. p. 45° (about). W. P. S.

**Chemical Examination of the Rhizome of *Cimicifuga racemosa*.** HORACE FINNEMORE (*Pharm. J.*, 1910, [iv], 31, 142-144).—Forty kilograms of the dried rhizomes and roots of *Cimicifuga racemosa* have been extracted completely by alcohol in a Soxhlet apparatus. By boiling the concentrated alcoholic extract with water, a resinous precipitate is obtained. From the aqueous filtrate, isoferulic acid, a minute amount of salicylic acid and a crystalline substance, m. p. 152°, have been isolated. From the resinous precipitate, formic, acetic, butyric, and palmitic acids, oleic and other more unsaturated acids have been isolated, and also a phytosterol, C<sub>27</sub>H<sub>45</sub>O, m. p. 138°, an alcohol (?), C<sub>18</sub>H<sub>33</sub>O<sub>4</sub>, m. p. 217-225°, and a substance, C<sub>15</sub>H<sub>25</sub>O<sub>4</sub>, m. p. 218-220°.

Evidence has also been obtained of the presence of a small amount of alkaloids in the drug. C. S.

**Fruit of *Menispermum Canadense*.** RAY E. NEIDIG (*Chem. News*, 1910, 102, 40-41).—The fruit is known under the name of "moo seeds," and is obtained from a vine growing to a height of about twelve feet. The berries are of a bluish-black colour, and resemble ordinary currants. They contain 61% of sugar, mainly dextrose, 5-38% of oil, 3-91% of ash, and 0-95% of nitrogen. The oil has D 0-9684, and is similar to castor oil; citric, oxalic, malic, and gallic acids are present in the fruits. W. P. S.

**Toxicity of Certain Salts towards Green Leaves.** LÉON MAQUENNE and EM. DEMOUSSY (*Compt. rend.*, 1910, 151, 178-182).—Observation of the blackening of leaves when immersed in salt solutions constitutes a simple method for determining the toxicity of substances towards protoplasm. In the case of copper sulphate, the reaction is very sensitive, the leaves showing a black border after twenty-four hours in a solution containing one part of copper in 5,000,000. Experimental data are given for various salts of the alkali metals and of ammonium, methylamine, and trimethylamine. Ammonium salts are much more toxic than those of potassium, sodium, or the two amines. W. O. W.

**Physiological Action of Calcium Cyanamide, and Compounds Derived from it.** FR. REIS (*Biochem. Zeitsch.*, 1910, 25, 477-493. Compare Abstr., 1910, i, 465).—Cyanamide, the active and important constituent of the commercial calcium cyanamide, is a powerful poison. It acts destructively, not only on animals, but on bacteria, moulds, germinating seeds, and also on growing plants, if it constitutes the only source of nitrogenous nourishment. Certain organisms can, however, live in a 0-1 per cent. solution of this compound. Sterile earth has a direct decomposing action on cyanamide solution; Dicyanodiamide, dicyanodiamidine, and diguanide in

0.1 per cent. solution are also assimilated by certain organisms, but no liberation of ammonia has been observed under these conditions. Cyanamide is doubtless valuable as an artificial manure, and in order to learn under what conditions it loses its poisonous properties and becomes converted into a source of nitrogen utilisable by higher plants, experiments were carried out on plants in clean quartz sand. Similar experiments were made, using dicyanodiamide, dicyanodiamidine sulphate, and diguanide. If the soil was watered with the solution before sowing the seed, and no other available source of nitrogen was provided, the poisonous action was marked. If the plants had grown considerably before the compounds were added to the soil, dicyanodiamidine sulphate could be used to a limited extent, whilst dicyanodiamide and diguanidine sulphate could not be used as fertilisers.

When calcium cyanamide acts as a fertiliser, it undergoes some changes in the soil. These are not completely understood, but the formation of urea may play an important part, and it has been shown to be formed from calcium cyanamide in the presence of ferric oxide.

G. S. W.

### Analytical Chemistry.

**Use of Sodium Carbonate for Oxidising Purposes.** EUGEN DEISS (*Chem. Zeit.*, 1910, 34, 781—782).—Sodium carbonate can be conveniently used for getting certain metals into a form in which they may be readily dissolved. The reaction takes place according to the equation  $M + CO_2 \rightleftharpoons MO + CO$ , where M is a bivalent metal. For analytical purposes it is best to use a mixture of sodium carbonate with either lime or magnesia, so that the mass simply sinters together and allows the carbon monoxide to escape freely.

The mixture (2 parts of magnesia to 1 part of sodium carbonate, or 1 part of magnesia to 2 parts of sodium carbonate) may be used for transforming such difficult soluble substances as silicon, titanium, tungsten, molybdenum, ferro titanium, manganese-titanium, ferrophosphor, etc., into a soluble form.

T. S. P.

**Estimation of Sulphur in Pyrites; Roasted Pyrites and Sulphates.** A. ZEHETMAYR (*Zeitsch. angew. Chem.*, 1910, 23, 1359—1360).—0.5 Gram of the finely powdered substance is placed in a combustion tube, 60—70 mm. long and 7—8 mm. wide, and closed at one end, mixed by the aid of a wire with twice the weight of pure reduced iron, and the contents are heated for a short time to redness. When cooled somewhat, it is dropped into a 200 c.c. generating flask containing 20—30 c.c. of water, which will cause it to crack. The flask is then fitted in the usual manner with a safety funnel and a short condenser furnished with a tube bent at right angles dipping into dilute potassium hydroxide. The sulphide formed is then decomposed by hydrochloric acid, and towards the last the

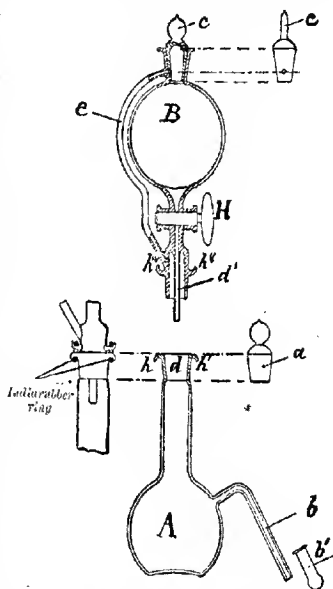
solution is boiled to expel the last traces of hydrogen sulphide. The liquid in the receiver is then titrated for hydrogen sulphide by the ordinary iodometric method.

L. DE K.

**Estimation of Sulphur Trioxide in Fuming Sulphuric Acid.**  
R. H. VERNON (*Chem. Zeit.*, 1910, 34, 792).—The apparatus consists of two parts, a dilution flask *A* with ground stopper *a*, and side-tube *b* fitted with a ground cap *b'*, also a separating funnel *B*, with stopcock, and a side-tube *c*; this connects the part of the funnel below the stopcock *H* with the upper stopper *c*. This stopper is also ground and hollow, and provided with a hole which allows communication of the funnel with the side-tube *e*.

*A* fitted with *a* and *b'* is weighed, and by means of a rubber tube fixed in the neck *d*, and applying suction, about 10 to 15 grams of fuming sulphuric acid are introduced into *A*, *b* being immersed in the acid. After again closing the flask with the stopper and cap, *b* is rinsed with water and wiped dry, and by re-weighing *A*, the exact amount of the fuming acid taken is ascertained. *B* is now filled half-way with water, and *H* is turned until the tube *d'* is completely filled with water, and then again turned off. Air is now blown through the upper part of the funnel to expel the water from *c*; the upper stopper *c* is then inserted in such a manner that there is no communication between the funnel and the side-tube *e*. The flask is now cooled by streaming water, which causes a diminished pressure, so that on removing the stopper *a*, no sulphuric fumes can escape.

After placing *a* in a beaker containing water, the funnel *B* is inserted in *A* and held by means of indiarubber rings through the hooks *hh'*, *h''*, and *h'''*. The apparatus is now held in an inclined position, and *H* is carefully opened so as to allow one drop of water to fall on the side of the neck of *A*. Owing to the explosive action of the water on the fuming sulphuric acid, a super-pressure is caused. *A* is again cooled, and another drop of water is introduced. If the pressure is so great that no water will enter, the stopper *c* is turned so that there is a momentary communication between the upper and





lower part of the apparatus. The operation is now repeated until the acid is fairly well diluted; the funnel *B* is made to communicate with the flask *A* by turning *c*, and the remainder of the water is then admitted, at first slowly, finally rapidly. If sulphuric fumes are still visible in *B*, the apparatus is turned upside down, and the acid entering *B* soon absorbs the fumes on shaking. The funnel is then disconnected. In order to remove any acid from tube *b*, *b'* is slightly loosened, and *b* is then inserted in the beaker containing the stopper *a*, and *b'* is detached by means of a glass rod. Every part of the apparatus, including the beaker, is now rinsed, and the liquid finally made up to 1 litre, when 20 to 30 c.c. are taken from the usual titration.

The following formulæ will be found convenient in calculating the results. Total % sulphur trioxide =  $80.07 \times b \times f/aG = X$ . Free sulphur trioxide =  $X - 80.07(100 - x)/18.016$ , in which *b* = c.c. of  $N/5$  sodium hydroxide; *f*, factor of the lye; *a*, the weight of the fuming acid, and *G*, the number of c.c. of acid titrated.

L. DE K.

**Estimation of Nitrogen by Kjeldahl's Method in Fatty Substances.** JOSEPH A. BROWN (*Chem. News*, 1910, 102, 51).—When applying the Kjeldahl process to substances rich in fat, such as cheese or milk, traces of slightly volatile fatty acids may still be present at the end of the digestion with sulphuric acid, and when distilling off the ammonia after adding excess of alkali, a troublesome frothing may occur.

This difficulty is entirely overcome by adding to the contents of the Kjeldahl flask, 100 c.c. of water, and then boiling down briskly to about 40 c.c. The fatty acids are then completely expelled.

L. DE K.

**Magnesium Ammonium Phosphate.** KURT BURE (*Zeitsch. anal. Chem.*, 1910, 49, 525—596).—A lengthy paper containing a review of the investigations of Neubauer, Järvinen, Schmitz, Jørgensen, and others as to the best method of obtaining an ideal magnesium ammonium phosphate precipitate. This compound may be obtained with  $1H_2O$  or  $6H_2O$ , but a mixture is frequently formed; this depends on the temperature.

Several tables and curves are given showing the solubility of the two compounds under various conditions, and the conductivity lines of the solutions.

The more important impurities which affect the analytical results are magnesium hydroxide, which is usually present when Jørgensen's directions are followed, and magnesium tetra-ammonium phosphate; this compound, the existence of which has been suspected by Neubauer, is, however, most likely magnesium ammonium phosphate, containing occluded ammonium phosphate.

The two crystallised compounds are decomposed by digestion with water at  $47-48^\circ$ ; the decomposition is retarded when magnesium mixture has been added.

L. DE K.

**The Precipitation of Ammonium Phosphomolybdate in Presence of Organic Acids.** G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], 19, i, 827—835).—Whilst the presence of tartaric or other

polybasic acids has sometimes been considered to hinder the precipitation of ammonium phosphomolybdate, other authors have recommended the addition of tartaric acid when it is required to precipitate phosphorus in the presence of much iron, as in the analysis of steel.

The two phosphate solutions employed were one of disodium phosphate in water and one of dicalcium phosphate in ammonium citrate, to which a little nitric acid had been added. To 10 c.c. of such a solution were added 30 c.c. of water, or 20 c.c. of water and 10 c.c. of a 34% solution of ammonium nitrate, followed by the organic acid, in quantity corresponding with that of the nitric acid usually added, and then, at a temperature near to boiling, variable quantities of solid ammonium molybdate. When this was dissolved, the precipitate was allowed to settle in the cold, and washed repeatedly with cold water in those experiments in which ammonium nitrate was not present, or with a solution of 5% ammonium nitrate and 4% nitric acid in other cases. The results are expressed in the form of tables and curves, and show that the presence of organic acids, glycerol, or sucrose does not hinder the precipitation if a sufficient quantity of nitric acid is present, and that organic acids may take the place of nitric acid, provided that a definite ratio of organic acid to precipitant is observed. Oxalic acid does not dissolve the phosphomolybdate except in hot concentrated solution, and then only with great difficulty, and tartaric acid in dilute solution is without influence. Fairly stable complex organic phosphomolybdic acids appear to exist. Sodium and calcium phosphates behave alike with respect to organic compounds. The results in the absence of ammonium nitrate are slightly low.

C. H. D.

**The Aluminium Reaction of Mercury Salts Insoluble in Water.** H. MUNT (*Pharm. Zentr.-h.*, 1910, 51, 677—678).—A slight modification of Reichard's test (this vol., ii, 655) so as to make it applicable to mercury salts insoluble in water.

Mercurous chloride gives the reaction when placed on aluminium foil and moistened with a drop of ammonia; after pressing with a glass rod, the foil is rinsed and allowed to dry, when the characteristic spot will become visible.

Mercuric sulphide gives the same reaction when moistened with either aqueous sodium hydroxide or dilute hydrochloric acid.

L. DE K.

**A Method of Treating and Preserving Large Quantities of Urine for Inorganic Analysis.** EDGAR A. SLAGLE (*J. Biol. Chem.*, 1910, 8, 77—79).—If sulphuric acid is added to the urine before evaporation, the residue dries hard without spitting, and can be removed from the dish (sometimes in a solid cake), and pulverised. This lends itself especially to estimation of inorganic constituents.

W. D. H.

**Komarowsky's Colour Reaction.** TH. VON FELLEBERG (*Chem. Zeit.*, 1910, 34, 791—792).—According to Komarowsky (*Abstr.*, 1903,

ii, 700), the "fusel" content of raw spirits may be estimated colorimetrically, as a red coloration is obtained on adding salicylaldehyde and sulphuric acid. According to the author, a similar reaction is obtained with the higher alcohols of the fatty series and their esters; also with the hydroaromatic alcohols, with phenols, and with those compounds which contain ethylene linkings in open chains or in hydroaromatic rings; tricyclic compounds, such as thujone, behave similarly. The exceptions are: the multivalent alcohols, the alcohols and phenols which contain carboxyl groups, the phenols which contain phenol groups in the ortho- or para-position, and the benzene derivatives with ethylene linkings which simultaneously contain a carboxyl group in the side-chain.

Brandy (cognac) is tested as follows: 10 c.c. of the distillate (obtained by rectifying the sample over potassium hydroxide and diluting the distillate to 30 vol.% alcoholic strength) are placed in a 100 c.c. flask, and 1 c.c. of a 1% alcoholic solution of salicylaldehyde is added; when much fusel oil is suspected, 5 c.c., diluted with 5 c.c. of 30% alcohol are added. Twenty c.c. of sulphuric acid are run down the side of the flask, and then mixed with the liquid by rotating gently. After forty-five minutes, 50 c.c. of 62% sulphuric acid are added, and the colour is compared with that of a liquid treated similarly and containing 2 parts of fusel oil in 1000 parts of 30 vol. % alcohol.

L. DE K.

**Gravimetric Estimation of Phenol.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1910, [ii], 14, 293—295).—The alkaline solution of bromine, prepared for the estimation of phenol according to Mascarelli's directions (*Abstr.*, 1909, ii, 353), contains sodium hypobromite as well as bromide and bromate.

When a solution of phenol at the ordinary temperature is treated with excess of a solution of sodium hypobromite, carbon tetrabromide is formed (compare Collie, *Trans.*, 1894, 65, 262), and the quantity of phenol found is only 22% of that calculated.

A comparison of estimations of phenol made with Mascarelli's solution and with a solution of sodium bromide (5 mols.) and bromate (1 mol.) shows that lower results are obtained with the former than with the latter solution, and that the difference is considerable when large amounts of the reagent are employed. The conclusion is drawn that Mascarelli's method becomes more accurate if his reagent is replaced by a solution of sodium bromide and bromate ( $3\text{NaBr} + \text{NaBrO}_3$ ).

E. H.

**Carbohydrate Metabolism. I. A Colorimetric Method of Estimating Sugar, and its Results.** LEONNARD WACKER (*Zeitsch. physiol. Chem.*, 1910, 67, 197—218).—A colorimetric method is described, by means of which it is claimed that sugar can be accurately estimated (error, 0.01%) in such small quantities of fluid as 0.3 to 0.4 c.c. Percentages as low as 0.00005 can be estimated. The method can be used for clinical purposes in estimating the sugar in human blood, and the figures given for the amount of sugar in normal blood (and urine) are higher than those stated by previous observers. In the case of blood, protein is removed by iron alum and

sodium carbonate. To the filtrate, phenylhydrazine-*p*-sulphonic acid and sodium hydroxide are added, and the red colour is compared with a colour scale previously made with the same reagents and a standard solution of dextrose. By the use of the method, the disappearance of sugar in blood allowed to stand (glycolysis) can be estimated; the sugar in blood and urine rises normally after carbohydrate food. It rises in both if the animal (rabbit) is cooled, and this "cold diabetes" is regarded as a factor in heat regulation. W. D. H.

**Influence of Iron on the Estimation of Glycogen.** EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1910, 27, 53—60).—See this vol., ii, 792.

**Test for Small Quantities of Cyanide.** GEORG LOCKEMANN (*Ber.*, 1910, 43, 2127—2128. Compare Berl and Delpy, this vol., ii, 661).—The substance to be tested is mixed with excess of dilute sulphuric acid and heated in a test-tube, the mouth of which is covered by a strip of filter paper (made by folding a piece of filter paper 1 dm. square into a strip  $2\frac{1}{2}$  cm. wide) which has been moistened with a drop of sodium or potassium hydroxide. The hydrogen cyanide liberated from the contents of the test-tube is absorbed by the alkali. After boiling for a short time, the paper is treated with a few drops of very dilute ferrous sulphate solution ( $\frac{1}{4}$ — $\frac{1}{2}$ %), and allowed to remain in contact with the air for some minutes in order partly to oxidise the ferrous hydroxide to ferric hydroxide. The strip is then again steamed for a short time over the test-tube, and finally treated with a few drops of strong hydrochloric acid. The presence of cyanide is indicated by the formation of Prussian blue.

An alternative method of testing is to moisten the filter paper originally with alkali hydroxide and yellow ammonium sulphide. Thiocyanate is formed by the hydrogen cyanide liberated from the contents of the test-tube, and is tested for in the usual way by hydrochloric acid and ferric chloride.

The presence of 0.03—0.04 mg. of cyanogen in the form of potassium cyanide, and of 0.2—0.3 mg. in the form of potassium ferrocyanide, can be detected. T. S. P.

**The Estimation of Lactic Acid by the Determination of the Amount of Acetaldehyde Obtainable by Scission Therefrom.** OTTO VON FÜRTH and D. CHARNASS (*Biochem. Zeitsch.*, 1910, 23, 199—220).—The authors have revised some of the previous work on the subject, and found that the volumetric method for estimating acetaldehyde by means of iodine and alkali (formation of isoform and titration of excess of iodine) is untrustworthy, except under very special conditions, such as the preservation of great dilution and low temperature. The potassium hydrogen sulphite method of Ripper for the estimation of aldehydes gives, however, trustworthy results. The oxidative scission of the aldehyde from lactic acid does not proceed quite quantitatively; by keeping to certain standard conditions, employing a certain form of distillation apparatus, and keeping the sulphuric acid concentration low, a definite percentage

of the quantitative yield of aldehyde can be obtained. The authors give in detail the method that can be employed for obtaining trustworthy quantitative results. S. B. S.

**Estimation of Methylamines in Presence of Large Quantities of Ammonia.** JEAN BERTHEAUME (*Compt. rend.*, 1910, 151, 146—149. Compare this vol., ii, 663).—The method already described for the estimation of mono-, di-, and tri-methylamine in presence of ammonia, not being applicable when the latter is in large excess, the author gives a modification based on Jarry's method for eliminating ammonia from mixtures of amines. Good results were obtained with a solution containing about 0.1% of the three methylamines in concentrated ammonia. W. O. W.

**\*Detection of Hexamethylenetetramine and Formaldehyde in Wine.** LÉON SURRE (*Ann. Palsif.*, 1910, 3, 292—293).—The test proposed depends on the blue coloration produced when hexamethylenetetramine and codeine are heated together in the presence of sulphuric acid. From 100 to 200 c.c. of the wine are acidified with sulphuric acid (about six drops) and distilled; the distillate is treated with calcined magnesia and again distilled, in this case about 10 c.c. of distillate being collected in a receiver containing 1 c.c. of ammonia. Hexamethylenetetramine is thus re-formed, whether the wine contained this substance or formaldehyde. The ammoniacal solution (distillate) is evaporated under reduced pressure over sulphuric acid. The residue is then rinsed with a small quantity of water into a porcelain basin and evaporated to dryness on the water-bath. After cooling, a small fragment of codeine is crushed and mixed with the residue in the basin, and two drops of a mixture of 85 c.c. of sulphuric acid with 15 c.c. of water are added. A blue coloration appears after heating the basin and its contents on a water-bath for five seconds should the wine contain hexamethylenetetramine. The sulphuric acid employed must be free from iron, otherwise it will give a blue coloration with codeine alone. The test will detect as little as 2 mg. of hexamethylenetetramine in 1 litre of wine. W. P. S.

**Differentiation of Iodine, Indican, and Scatole in Jaffé's Indican Reaction.** BODO SPIETHOFF (*Chem. Zentr.*, 1910, ii, 45; from *Münch. med. Woch.*, 1910, 57, 1066—1067).—The presence of indican or scatole in urine is a source of error in many iodine reactions, and, conversely, the presence of iodine interferes with the Jaffé test for scatole. The error is avoided when the liquid after shaking with chloroform is passed through a filter. The blue colouring matter is deposited on the filter, and, as these filters are permanent, a fair idea as to quantity present may be obtained by comparison experiments. If scatole is present besides iodine, the blue starch-iodine colour disappears on drying the filter; the red scatole deposit remains at the bottom of the filter. In the presence of indican, the filter remains blue on warming. L. DE K.

## General and Physical Chemistry.

**Lehmann's Anisotropic Liquids.** GEORGES FRIEDEL and F. GRANDJEAN (*Compt. rend.*, 1910, 161, 327—329, 442—444).—A discussion of the optical properties of liquid crystals. The authors show that some of the phenomena exhibited by anisotropic liquids may be explained by regarding a thin layer of such a liquid as consisting of two films showing double refraction and enclosing a liquid having a very high rotatory power.

In the second paper, the authors discuss the appearances presented by Lehmann's liquid crystals when viewed under the microscope between nicol prisms, and arrive at the conclusion that these compounds are examples of a new state of matter entirely distinct from crystalline substances or isotropic liquids. W. O. W.

**Optics of Liquid Crystals.** ERNST DORN (*Physikal. Zeitsch.*, 1910, 11, 777—780).—The refractive indices for both the ordinary and extraordinary rays have been measured in the case of the liquid crystalline substances, ethyl ethoxybenzylideneamino- $\alpha$ -methylcinnamate and ethyl ethoxybenzylideneamino- $\alpha$ -ethylcinnamate. Data were obtained for the wave-lengths  $\lambda = 6708, 5893$ , and  $5461$ ; for  $\lambda = 5893$  determinations were made at different temperatures. The polarisation effects observed in the case of cholesteryl propionate are also described in detail. H. M. D.

**Optical Investigation of an Optically Active Liquid Crystalline Substance.** FELIX STUMPF (*Physikal. Zeitsch.*, 1910, 11, 780—784).—Measurements of the refractive index for the ordinary and extraordinary rays have been made in the case of amyl *p*-cyano-benzylideneamincinnamate. These show the magnitude of the dispersion and the influence of temperature on the refraction. The rotation of the plane of polarisation parallel to the optical axis, which is so markedly characteristic of liquid crystals, has also been examined in detail. The appearance of the substance under the ultra-microscope indicates that it is not homogeneous. H. M. D.

**Molecular Refraction of the Isomeric Hydrocarbons,  $C_{10}H_{22}$ .** PAUL ROHLAND (*Zeitsch. physikal. Chem.*, 1910, 74, 382—384).—The isomeric hydrocarbons, *n*-decane, m. p.  $173^\circ$ , and diisooamyl, m. p.  $163^\circ$ , although they melt at different temperatures, have practically the same density and molecular refractivity. These facts are difficult to reconcile with the ordinary structure hypothesis, according to which a difference in constitution is associated with a difference in many physical properties. It is probable that the higher boiling point of *n*-decane is due to a certain degree of polymerisation. G. S.

**Physical Properties of Binary Mixtures of Liquids.** J. C. HUBBAARD (*Zeitsch. physikal. Chem.*, 1910, 74, 207—232).—The specific volumes at  $25^\circ$  and  $35.17^\circ$  or  $50^\circ$ , and the refractivities for the C, D, F, VOL. XXVIII. II. 22

and *G* lines of the following six binary mixtures—carbon disulphide-methylal, carbon disulphide-acetone, chloroform-acetone, ethyl iodide-ethyl acetate, acetic acid-benzene, and carbon tetrachloride-benzene—have been measured. Special precautions were taken in purifying the materials. In each case, mixtures containing varying proportions of the components were investigated. The choice of substances was determined by the fact that the partial pressures of binary mixtures containing them have already been measured by von Zawidzki (compare Abstr., 1901, ii, 6).

The variation of these properties (including the partial pressures) from the additive values are given in tabular form and are also represented graphically, the differences being plotted as ordinates against the composition of the mixtures as abscissae. As regards the specific volumes, the deviations from additive behaviour increase in absolute value as the temperature rises. A rather doubtful exception to this rule is the chloroform-acetone mixture. Further, the deviation of the specific volume has the same sign in each case as that of the vapour pressure at the same temperature. The deviations of the refraction from the additive values have for the systems carbon disulphide-methylal, carbon disulphide-acetone, and carbon tetrachloride-benzene the same sign, and in the other cases the contrary sign, to the deviations of the vapour pressure and specific volume. The absolute values of the refractivity deviations increase as the wave-lengths diminish.

G. S.

**Influence of Complex Formation on the Volume and Refractivity of Dissolved Substances.** EBERHARD KIMBACH and R. WINTGEN (*Zeitsch. physikal. Chem.*, 1910, 74, 232–253).—The object of the investigation was to find if volume and refractivity measurements can be employed usefully to detect the formation of complexes between two substances in aqueous solution. It was, however, found that these methods are much less advantageous than those in general use.

For mixtures of certain salts, such as potassium and sodium chlorides, for which no complex formation is to be anticipated, the deviations from additive behaviour are less than the experimental error, and are very small even for mixtures of aluminium sulphate and alkali sulphates.

The deviations are noticeable, but are still comparatively small, for mixtures containing silver-potassium cyanide, mercuric potassium iodide, etc. As even these slight differences might be due to changes of ionisation, a number of experiments were made with isohydric mixtures of molybdic acid and other acids, both inorganic and organic. For mixtures containing phosphoric, arsenic, and iodic acid respectively, the deviations scarcely exceed the experimental error, although these substances are known to form complexes with molybdic acid. When organic acids which do not contain a hydroxyl group are used, the deviations in the case of refractivity are within the limits of experimental error, but are considerable for hydroxy-acids, corresponding with the fact that the latter form complexes with molybdic acid. No error arises in these measurements owing to a change in the molybdic

acid, as its molecular refractivity remains practically constant on dilution. The volume relations for the hydroxy-acids are rather less definite than the refractivity relations.

G. S.

#### Long-waved Portion of the Banded Nitrogen Spectrum.

REINER VON DER HELM (*Zeitsch. wiss. Photochem.*, 1910, 8, 405—432).

—To obtain information relating to the structure of banded spectra, the author has investigated the banded spectrum of nitrogen between  $\lambda = 5000$  and  $\lambda = 6900$ . The wave-length measurements are discussed in detail with reference to the formulæ of Deslandres and Thiele.

H. M. D.

#### Intensity Minimum of the Cyanogen Group of Bands,

$\lambda = 3883.558$ . J. W. HAFERKAMP (*Zeitsch. wiss. Photochem.*, 1910,

9, 19—36).—The influence of pressure on the distribution of the light intensity in the third group of bands in the cyanogen spectrum has been examined in detail. The observed variations are interpreted in terms of the electron theory.

H. M. D.

#### Position of Ultimate Rays in Spectral Series.

ANTOINE DE GRAMONT (*Compt. rend.*, 1910, 151, 308—311. Compare Abstr., 1907,

ii, 517).—Two types of spectra have been recognised in the study of the ultimate rays or lines of great persistence. In one, the lines do not fall into regular periodic series, but can be arranged in lines and parallel columns showing constant differences in wave-lengths, in this respect showing the regularities discovered by Kayser and Runge in the spectra of tin, lead, bismuth, antimony, and arsenic. The second type shows series converging to a finite limit. A principal series has been recognised in the ultimate rays for lithium, sodium, potassium, rubidium, and caesium, but in the case of aluminium, indium, and thallium the principal series cannot be recognised; some of the lines for these metals appear to belong to a secondary series. Zinc, cadmium, and mercury show lines possibly belonging to an undiscovered principal series.

W. O. W.

#### Emission and Absorption of Luminous Hydrogen.

RUDOLF

LADENBURG (*Ber. Deut. physikal. Ges.*, 1910, 12, 549—564).—In part

polemical against Pflüger (*ibid.*, 1910, 12, 208). In reference to the

relationship between the emission and absorptive capacity of luminous

hydrogen, new measurements have been made which confirm the

author's previous conclusion that the ratio of the emissive power to the

absorptive power varies appreciably within the limits of the

band  $H_{\alpha}$ .

H. M. D.

#### Spectra of the Metals in the Electric Arc. VIII. Spectrum

of Uranium. B. HASSELBERG (*K. Svenska Vet.-Akad. Handl.*, 1910,

45, 3—69).—A detailed account is given of wave-length measurements

in the arc spectrum of uranium from  $\lambda = 3528$  to  $\lambda = 5871$ . The

apparatus and the method were those previously used by the author in

the investigation of the spectra of molybdenum (Abstr., 1903 ii,

706) and tungsten (Abstr., 1905, ii, 129).



From a comparison of the uranium and solar spectra, it is found that 75% of the principal uranium lines are absent from the solar spectrum.

On account of the very small intensity of the lines in the solar spectrum, which appear to coincide with the remaining uranium lines, the author considers that the actual coincidence is not established. The evidence points therefore to the absence of uranium in the sun.

H. M. D.

**Uranium and Neodymium Aggregates.** W. W. STRONG (*Physikal. Zeitsch.*, 1910, 11, 668—671).—Observations are recorded showing the changes which occur in the absorption spectra of uranyl and neodymium salts when free acids are added to their aqueous solutions. The observations are interpreted in terms of the solvate theory, and it is supposed that the envelope of solvate molecules which surrounds the active nucleus may be of such dimensions that changes in the outer layers of the envelope have little influence on the absorption bands.

The bands in the spectra of uranyl salts are in no way similar to the bands furnished by uranous salts. The "water bands" and the "alcohol bands" of neodymium do not follow Beer's law, and the two series of bands are not affected in the same way by a change of temperature.

H. M. D.

**Anomalous Rotatory Dispersion. II.** Leo TSCHUGAEFF and A. OGORONNIKOFF (*Zeitsch. physikal. Chem.*, 1910, 74, 503—512).—In addition to the three compounds already referred to (compare Abstr., 1909, ii, 631), the following have now been found to show anomalous rotatory dispersion: methyl *l*-menthyl xanthate,  $\text{MeS}\cdot\text{CS}\cdot\text{O}\cdot\text{C}_{10}\text{H}_{19}$ ; methyl, ethyl, and *n*-propyl *d*- and *l*-bornyl xanthates; *l*-menthylthiourethane,  $\text{CSPh}\cdot\text{NPh}\cdot\text{CO}\cdot\text{C}_{10}\text{H}_{19}$ ; *l*-menthyl, *l*- and *d*-bornyl, and *l*-fenchyl dithiourethanes,  $\text{CSPh}\cdot\text{NPh}\cdot\text{CS}\cdot\text{OR}$ .

One of the objects of the investigation was to compare anomalous rotatory dispersion with the absorption of light. The latter was therefore also measured, but in the visible region only, with a König-Martens spectrophotometer. The results show that there is a close connexion between these two factors. The rotation curves for the methyl and ethyl esters of *l*-bornyl xanthate are very similar, as are the absorption curves, whilst for *l*-bornyl dixanthate both the rotation maximum and the absorption are displaced towards the red with reference to those for the two esters. Exactly corresponding results were obtained with the thiourethane derivatives.

G. S.

**Determination of the Optical Constants of Metals from Polarisation Measurements.** W. VON ULJANIN (*Physikal. Zeitsch.*, 1910, 11, 784—789).—Equations are deduced which give the relationship between the polarisation of the light reflected from metals and the optical constants. Measurements of the polarisation have been made in the case of mercury, nickel, and aluminium, and from these the refractive indices and extinction coefficients for red, yellow, and blue rays are calculated. It is shown that the polarisation effect is

only slightly influenced by considerable changes in the optical constants, but the author believes that this method of measurement should be of particular importance in the case of ultra-red rays.

H. M. D.

**Ultra-violet Fluorescence and Chemical Constitution of Cyclic Compounds.** HEINRICH LEY and K. VON ENGELHARDT (*Zeitsch. physikal. Chem.*, 1910, 74, 1—64).—A more detailed account of work already published (compare Abstr., 1908, ii, 911). The vinyl and  $\text{CH}_2\text{C}$  groups, like the methoxyl and hydroxyl groups, act as auxofluors, and have also a strong bathofluor influence. From a qualitative point of view, the effect of two substituents in the benzene nucleus is additive, but there are certain exceptions in the case of unsaturated groups. Substitution in a saturated side-chain causes little or no spectral displacement of the benzene fluorescence, but when two unsaturated groups are attached to the same carbon atom, the results are anomalous.

G. S.

**Simple and Combined Photochemical Reactions.** ALFRED BENRATH (*Zeitsch. physikal. Chem.*, 1910, 74, 115—124).—A purely photochemical reaction is one which does not proceed in the dark, and when exposed to light the rate is proportional to the amount of light energy absorbed. It follows that with constant illumination the rate of the reaction is proportional to the time of exposure. In a previous paper (compare Abstr., 1909, ii, 847) it has been shown that the reduction of ferric chloride by alcohols is a simple photochemical reaction, and the same is now shown to be the case when the reduction is affected by tartaric, citric, and oxalic acids and by glycerol. As before, a mercury vapour lamp was used as the source of illumination. The rate of reduction in quartz vessels is about double that in glass vessels, a result ascribed to the absorption of a considerable part of the light energy by the glass. The relative activities of malic, citric, lactic, tartaric, and mandelic acids as reducing agents are as 1:1.68:1.81:2.47:3.57. The reduction of ferric chloride by hydroxyacids is much slower in acetone than in water.

A catalytic light reaction is one which proceeds slowly in the dark and is accelerated by light. It is shown, both by calculation of the results of Roloff (compare Abstr., 1894, ii, 221) on the oxidation of oxalic acid by bromine and by direct experiments with bromine and tartaric acid, that the reduction of  $\text{Br}_2$  to  $2\text{Br}^{\cdot}$  is a catalytic light reaction, as it proceeds more rapidly in light than in darkness, whilst the simultaneous reduction of  $\text{Br}_2$  to  $3\text{Br}^{\cdot}$  is a purely photochemical reaction. The whole process in this case may be termed a combined light reaction.

G. S.

**Mechanism of Photochemical Reactions and the Formation of Vegetable Substances; Decomposition of Sugar Solutions.** DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, 151, 395—397. Compare this vol., i, 349, 543; ii, 564, 606).—This paper contains a discussion of results already published, and the results of analysis of the gaseous products obtained when sugar solutions are exposed to the light from a quartz-mercury lamp.

Carbon monoxide, carbon dioxide, methane, and hydrogen were obtained in each case. Dextrose gave equal volumes of carbon monoxide and methane with about six times as much hydrogen. Lævulose gave ten times as much carbon monoxide as methane. Maltose gave the same proportions as dextrose, whilst sucrose behaved as a mixture of dextrose and lævulose.

W. O. W.

**Photochemical Decomposition of Alcohols, Aldehydes, Acids, and Ketones.** DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1910, 151, 478—481. Compare preceding abstract).—The results are given of analyses of the mixed gases obtained by exposing a number of substances to the action of light from a quartz-mercury lamp. The compounds examined included the first three members of the aliphatic saturated alcohols, aldehydes, and acids, also formamide and diethyl ketone. Acetone is decomposed very rapidly by ultra-violet light, giving carbon monoxide (49 vols.), methane (5 vols.), and ethane (46 vols.); in aqueous solution carbon dioxide is also formed. Solid calcium lactate gives the same gases with hydrogen; the proportion between this and the carbon dioxide is about the same as when these gases are produced in the butyric fermentation. Solid carbamide gives carbon dioxide, hydrogen, and methane; an aqueous solution evolves only the latter two, and becomes ammoniacal.

W. O. W.

**Chemical Changes Produced by Different Kinds of Rays.**  
**III. The Change of Benzoic Acid into Salicylic Acid in Sunlight.** CARL NEUBERG (*Biochem. Zeitsch.*, 1910, 27, 271—272. Compare Abstr., 1903, ii, 540).—If a solution of benzoic acid containing ferric chloride is exposed to sunlight, the violet colour characteristic for salicylic acid develops. Thirteen % of the benzoic acid was thus oxidised during sixteen days in June in Berlin. With ferrous sulphate the change of benzoic into salicylic acid also takes place, but it is slower. In artificial light the change can also take place.

S. B. S.

**Photoelectric Experiments with Anthracene.** ALFRED BYK and H. BORCK (*Ber. Deut. physikal. Ges.*, 1910, 12, 621—651).—Experiments are described which show that anthracene, although an insulator, is a photo-electrically active substance. This fact is connected with the observed photo-polymerisation of anthracene, and the action of light is supposed to consist in the removal of electrons, or in the splitting up of the neutral anthracene molecules into two oppositely-charged portions.

H. M. D.

**Tables of Constants of Ionisation and Radioactivity.** T. H. LEBY (*Le Radium*, 1910, 8, 189—196).—These tables comprise values of (1) the coefficient of recombination,  $\alpha$ , for different gases and its variation with pressure and temperature; (2) the coefficient of diffusion of ions produced by different agencies in different gases by the  $\alpha$ -rays, and its variation with the pressure for ions produced by the  $\beta$ - and  $\gamma$ -rays; (3) the mobility of ions for air and various dry gases, and

the effect of temperature and pressure; and of the ions in non-conducting liquids and solids and in flames; (4) the ratio  $v_2/v_1$  of the expansion necessary to produce condensation in gases and vapours ionised by X-ray and the rays of radium; (5) the charge  $NE$  of electrolytic and gaseous ions and of the ionic charge  $e$  as determined by various methods; (6) the number of molecules in a gram-molecule of gas; (7) the ratio  $e/m$  of the negative electron as determined for cathode rays and secondary rays and from the Zeeman effect, and the variation of the ratio with velocity; (8) values of  $RH$ , the magnetic deviation, and  $v$ , the velocity of cathode rays; (9) ranges and velocities of  $\alpha$ -rays, the number emitted from radium, the ratio  $e/m$  of  $\alpha$ -rays, the absorption in gases and metals, the number of ions produced by an  $\alpha$ -particle, its variation with velocity, and the relative total ionisation in different gases (also for  $\beta$ ,  $\gamma$ , and X-rays); (10) the disengagement of heat from radium, its emanation, and thorium; (11) the constant of the radium emanation, its volume, vapour pressure, and coefficient of diffusion; (12) radioactive and atomic constants.

F. S.

**The Energy of the Rays of Radium.** WILLIAM DUANE (*Compt. rend.*, 1910, 151, 471—473).—A holometer, radiometer, thermoelectric pile, and differential gas thermometer were all found unsatisfactory in showing the energy of the rays of radium, but results were obtained with the sensitive calorimeter previously described (*Abstr.*, 1909, ii, 534). A tube containing the radium emanation was used as the source, and the rays passed through two thin mica windows, thin enough to allow the  $\alpha$ -rays of radium-C to penetrate, but not those of the emanation or of radium-A. They fell upon the glass walls of an exhausted glass tube which was inserted into the calorimeter. A clear effect was produced which was stopped completely by two thin aluminium leaves. Hence the  $\beta$ - and  $\gamma$ -rays do not produce any appreciable effect. It is hoped in this way to obtain a measure of the energy of the  $\alpha$ -rays throughout their range.

F. S.

**The  $\beta$ -Rays of Radium at its Minimum Activity.** LÉON KOLOWRAT (*Compt. rend.*, 1910, 151, 525—528).—The existence of a very absorbable  $\beta$ -radiation, specific to radium itself (Hahn and Meitner, *Abstr.*, 1909, ii, 954), has been confirmed by new experiments. A small quantity of a radium salt was heated on a platinum plate, and its  $\beta$ -activity measured after different periods, and also the absorption coefficient of the  $\beta$ -rays by interposing a series of eight aluminium screens of graduated thickness. The value of the absorption coefficient  $\mu$  rapidly decreased during the first few hours after heating from an initial value of about  $200 \text{ (cm.)}^{-1}$  to a final value of 60. The value of the initial  $\beta$ -activity, obtained by extrapolating the curves back to zero thickness, was about 2% of the final equilibrium  $\beta$ -activity. Hahn (with different measuring arrangements) had found it 7%, and for the value of  $\mu$   $312 \text{ (cm.)}^{-1}$ . The results are fully in accord with the hypothesis of the existence of a very absorbable  $\beta$ -radiation due to radium itself.

F. S.

**The Disengagement of Heat in a Mixture of Radium and of a Phosphorescent Salt.** WILLIAM DUANE (*Compt. rend.*, 1910, 151, 379—381).—With the very sensitive calorimeter previously described (*Abstr.*, 1909, ii, 534), a feeble development of heat has been detected from a phosphorescent salt one or two hours after it has been exposed to light. In most cases no effect is produced after twenty-four hours, but in others the development of heat persists even after the phosphorescence has become invisible. Experiments were made on the amount of heat developed from a preparation containing radium, alone and mixed with phosphorescent zinc sulphide. The heat evolution is proportional to the  $\gamma$ -activity of the preparation in each case, so that the presence of the phosphorescent salt is without effect. In other experiments the radium was contained in a sealed tube, and the  $\beta$ - and  $\gamma$ -rays allowed to produce phosphorescence in willemite or barium platinocyanide. The same development of heat was observed as when no phosphorescent salt was present. Hence there is no appreciable absorption or evolution of energy by the phosphorescent salt due to chemical reactions.

F. S.

**Radioactive Recoil Products (Projections).** LOUIS WERTHEIMSTEIN (*Compt. rend.*, 1910, 151, 469—471. Compare this vol., ii, 476).—A disk of glass, rendered active by immersion in the radium emanation, was silvered in a silvering bath and dried. It was mounted opposite to a brass plate in a vacuum. It was found that a thickness of silver of the order of  $10\ \mu$  allowed about 60% of the recoil product to pass through, but a thickness of  $20\ \mu$  arrested it completely. The range of the recoiling particles was found to be about 0.7 mm. in hydrogen at atmospheric pressure, or six times the range in air, which is nearly the same ratio as is found for the range of the  $\alpha$ -particle. The range of the recoiled particles or their number appears to diminish as the direction of emission from the surface becomes more oblique. A series of parallel disks charged alternately positively and negatively was placed in an exhausted vessel containing radium emanation and air at known low pressure. It was found that the active deposit on the positive plates increased rapidly with the distance apart of the plates up to a distance corresponding with the range of the recoiling particle, and then continued to increase about twenty times more slowly. This shows that recoil plays a part in the rendering active of surfaces by the emanation. Evidence of a strong ionisation produced by particles of radium-D recoiling from radium-C has been obtained. The total ionisation between two parallel plates, one coated with radium-C, increases rapidly with their distance apart up to the distance corresponding with the range of the recoiling particle, but further experiments are necessary to establish such an effect.

F. S.

**Metallic Radium.** MME. MARIE CURIE and ANDRÉ DEBIÈRE (*Compt. rend.*, 1910, 151, 523—525).—Preliminary experiments with barium, using about 0.1 gram of material, by Guntz's method gave the necessary conditions and experience for the preparation of radium. The amalgam was obtained by electrolysis of a solution of 0.106 gram

of perfectly pure radium chloride with cathode of mercury (10 grams) and anode of platinum-iridium. After electrolysis, the solution contained 0.0085 gram of this salt. The amalgam was quite fluid, whereas with barium under similar conditions it is partly crystalline. The dried amalgam was transferred to an iron boat and heated cautiously in a quartz tube in a current of pure hydrogen, purified by passage through the walls of a platinum tube heated in an electric furnace. The temperature of the boat was determined by a thermocouple. Most of the mercury was distilled at 270°. At 400° the amalgam became solid, and its melting point rose progressively as the mercury was driven off to 700°, when no more mercury volatilised, but the radium itself commenced to volatilise and to attack the quartz tube energetically. The boat now contained a brilliant white metal, fusing sharply in the neighbourhood of 700°, which was considered to be pure radium. It adhered strongly to the iron, and blackened immediately on exposure to the air, probably forming the nitride. A particle falling on white paper produced a blackening analogous to a burn. The metal decomposed water energetically, and dissolved for the most part, showing that the oxide is soluble. The small, black residuum (nitride) dissolved completely in a very little hydrochloric acid, showing that no mercury was present. The penetrating rays from the boat containing the metal, sealed in a glass tube, showed the normal increase following the law of production of the emanation. Owing to metallic radium being much more volatile than barium, it is proposed to purify it by sublimation in a vacuum. F. S.

**Radio-Lead.** H. HERCHFINKEL (*Le Radium*, 1910, 8, 198—200).—Numerous unsuccessful attempts to concentrate the radium-D in radio-lead are described. The raw material is lead nitrate of an activity three to four times that of uranium oxide. Various metals were immersed in the solution. The chloride and bromide were fractionally crystallised. Cerium nitrate was precipitated in the nitric acid solution. Iron was precipitated in the solution as the basic acetate, and again barium sulphate by addition of barium nitrate and sulphuric acid. Digestion of the solution with animal charcoal, excepting one case which could not be repeated, resulted in no concentration of the radium-D. The active metallic lead was distilled at 600—700°, but the portion volatilising was not permanently active. Possibly a concentration in the non-volatile part might be effected in this way. A few per cent. of zinc was added to the lead and distilled off at about 1250°, and the distillate possessed a constant activity a little greater than the initial substance. A triple alloy of zinc and silver formed with the lead contained only polonium. No successful method of concentration was found. F. S.

**Occurrence of Free Electrons in Chemically Inert Gases at Atmospheric Pressure.** J. FRANCK (*Ber. Deut. physikal. Ges.*, 1910, 12, 613—620).—Measurements of the velocity of the negative ions in chemically pure argon and nitrogen indicate the presence of free electrons. If small quantities of oxygen are mixed with these inert gases, the mobility of the negative ions is reduced to about 1% of

its value in the pure gases. The addition of chlorine, water or nitric oxide causes a similar reduction in the ionic mobility, and it is supposed that these substances combine with the free electrons and thus yield negative ions which are much less mobile than the free electrons.

H. M. D.

**Decomposition of Water Vapour by the Silent Electrical Discharge.** MIAOSLAW KERNBAUM (*Compt. rend.*, 1910, 151, 319—322. Compare Abstr., 1909, ii, 364, 714, 717).—A brush discharge was made to play in an atmosphere of water vapour free from air. Hydrogen and hydrogen peroxide were produced, probably in accordance with the equation  $2\text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{H}_2$ . The amount of hydrogen obtained depends largely on the condition of the platinum electrode, a new point giving 2.4% in the first experiment, 0.8% in a second, and practically none in a third. The results are analogous with those obtained in the action of ultra-violet light and the  $\beta$ -rays of radium on water, and appear to be due to ionisation produced by cathode radiation.

W. O. W.

**Conduction of Electricity in Crystals at High Temperatures.** CORNELIO DOELTER (*Monatsh.*, 1910, 31, 493—555. Compare Abstr., 1906, ii, 665; 1908, ii, 178, 839; Königsberger, Abstr., 1909, ii, 289).—Electrolytic as well as metallic conduction can occur in crystals. The conductivity temperature curves are not sufficient to distinguish between the two types of conductivity; determinations of polarisation are essential. As a result of examination of these two properties, substances are divided into three classes: 1. Crystals which give no polarisation and in which the conductivity increases with the temperature. To this group belong rutile, tinstone, chrysoberyl, and probably wolframite. 2. Substances which show slight polarising effects at very high temperatures; for example, adularia and albite. 3. Crystals which show appreciable polarisation at high temperatures; for example, sapphire, barytes, topaz. In these cases the conductivity diminishes as the temperature rises.

The most trustworthy conclusions can be drawn by determining both resistance and polarisation at temperatures until the mass is quite molten.

In the case of silicates, the polarisation is small even in the fused state (for example, only a few tenths of a volt), and this is accompanied by a high resistance which is attributed to the high viscosity rather than to low dissociation. The conductivity becomes greater at temperatures much above the melting point. The conductivity of albite, in spite of its high viscosity, is some ten times as large as that of labradorite at a temperature of 1200—1300°. The ratio of conductivities of albite solid at 1000° and albite liquid at 1250° is 1:2, and the curve, using the Kohlrausch-Arrhenius method, for the transition solid to liquid is a straight line.

Electron conductivity is possible in the liquid state, and probably many sulphides, sulphonic acids, and antimonite behave in this way.

Difficulties are met with in the case of quartz; many specimens show high conductivities, but this is due to secondary causes, as in some

cases it has been found possible to obtain a metal (sodium) by electrolysis.

The following division of crystals is given: *A.* Those which exhibit metallic conductivity at all temperatures without electrolytic conductivity—lead sulphide, antimony sulphide, ilmenite, pyrites, and magnetite.

*B.* Crystals which are insulators at the ordinary temperature, but which exhibit metallic conductivity at rather higher temperatures; for example, zinc blende, molybdenum sulphide, pyrites, antimony pyrites, fahlore. *C.* Crystals, such as tinstone and chrysoberyl, in which polarisation has not been definitely determined, but which probably exhibit both metallic and electrolytic conductivity. *D.* Crystals which are insulators at the ordinary temperature, but are conductors at high temperatures and show appreciable polarisation; for example, metallic chlorides and iodides, barium sulphate, sapphire, and silicates.

The transition from the amorphous to the crystalline state is usually accompanied by a break in the temperature conductivity curve.

In the case of polymorphous substances, the form which is the more stable at high temperatures has the greater conductivity.

J. J. S.

**Abnormal Action of the Gas Electrode in the Determination of the Concentration of Hydrogen Ions by Electric Measurement.** J. E. ENKLAAR (*Chem. Weekblad*, 1910, 7, 733—735).—The results obtained when the concentration of the hydrogen ions in a solution of chloral hydrate containing a neutral salt is determined are abnormal, and comparable with those furnished by a strong mineral acid. The author attributes this abnormality to displacement of chlorine by hydrogen, with formation of acetaldehyde and hydrochloric acid.

A. J. W.

**Hydrolysis of Iodine and of Bromine.** WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1910, 32, 932—938).—The work described in this paper was carried out in order to ascertain the cause of the conductivity of aqueous solutions of iodine. From calculations based on Sammet's determinations of the equilibrium constants (*Abstr.*, 1906, ii, 153), the conclusion was drawn that both the following reactions must be considered: (1)  $I_2 + H_2O = H^+ + I^- + HIO$ , and (2)  $3I_2 + 3H_2O = 6H^+ + 5I^- + IO_3^-$ . It was expected that the conductivity would at first rise rapidly in accordance with (1) and then continue to rise slowly in accordance with (2), and this has been confirmed.

Determinations have been made of the solubility of iodine and bromine in water, and of the conductivity of the solutions at 25°. The results show that iodine is soluble to the extent of 1.32 millimols.  $I_2$  per litre, and bromine to the extent of 0.21 mol.  $Br_2$  per litre. The hydrolysis constants:  $(H^+)(I^-)(HIO)/(I_2)$  and  $(H^+)(Br^-)(HBrO)/(Br_2)$  have been found to be  $0.6 \times 10^{-12}$  and  $2.4 \times 10^{-8}$  respectively.

E. G.



**Conductivity and Ionisation of Potassium Tri-iodide, and the Equilibrium between Iodine, Iodide, and Polyiodides in Aqueous Solution.** WILLIAM C. BRAY and G. M. J. MACKAY (*J. Amer. Chem. Soc.*, 1910, 32, 914—932).—This investigation was carried out with the object of determining the equivalent conductivity of the tri-iodide ion,  $I_3^-$ , a knowledge of which is required in the study of the equilibrium between iodine, potassium iodide, and polyiodides in aqueous solution. The conductivity of potassium iodide solutions of concentration between 0.1*N* and 0.001*N*, and of the same solutions saturated with iodine have been determined at 25°.

The results show that the degree of ionisation of potassium tri-iodide in dilute solutions is practically identical with that of potassium iodide up to a concentration of 0.1*N*, and that the values of  $\Lambda_1$  and  $\Lambda_{I_3}$  at 25° are 76.5 and 41.0 respectively, that of potassium iodide being regarded as 74.8. Burgess and Chapman (*Trans.*, 1904, 85, 1305) found by means of transference experiments that  $\Lambda_{I_3}/\Lambda_1 = 0.566$ , whence if  $\Lambda_1$  is taken as 76.5,  $\Lambda_{I_3}$  has the value 42.5. An intermediate value, 41.5, has therefore been adopted as the most probable value of  $\Lambda_{I_3}$ . It has also been found that in potassium iodide solutions saturated with iodine the ratio  $C_1/C_{I_3}$ , which, according to the law of mass action, should be a constant, decreases from 1.16 to 0.99 between 0.0*N* and 0.1*N*; the effect due to the presence of potassium iodide, which is known to occur in more concentrated solutions, is therefore apparent also in very dilute solutions.

An attempt has been made to determine the composition of concentrated solutions of potassium iodide saturated with iodine. An exact solution of the problem is not possible, but it appears that the ratio of "activity" (Lewis, *Abstr.*, 1908, ii, 16) to concentration for the iodide ion is nearly independent of the concentration, that this ratio for the tri-iodide ion decreases rapidly in concentrated solutions, and that higher polyiodide ions show this abnormality in a still higher degree. In a *N*-solution of potassium iodide, saturated with iodine, the concentration of  $KI_3$  is calculated to be about 0.08 molal if this is the only higher polyiodide present. E. G.

**Conductivity of Some Concentrated Aqueous Solutions at Zero.** W. H. SLOAN (*J. Amer. Chem. Soc.*, 1910, 32, 946—949).—On determining the conductivity of concentrated aqueous solutions of potassium iodide at 0°, unexpected values were obtained. These results have been confirmed, and the conductivities of concentrated solutions of potassium bromide, sodium nitrate, ammonium nitrate, silver nitrate, and cupric nitrate have also been determined. The results are tabulated and plotted as curves.

The values obtained with potassium iodide differ from those found by Jones and Douglas (*Abstr.*, 1902, ii, 59), but the type of curve agrees closely with that of Kahlenberg (*Abstr.*, 1901, ii, 540). The values resemble in some respects those obtained for certain salts in methylamine and liquid ammonia (Franklin and Gihbs, *Abstr.*, 1907, ii, 840; Franklin, *Abstr.*, 1909, ii, 957).

The conductivity of the potassium bromide solutions resembles that of the potassium iodide solutions, but the limited solubility of the

former salt excluded the possibility of examining very concentrated solutions. The other salts did not give any exceptional values except in the case of cupric nitrate, in which the specific conductivity increased up to a certain point with the dilution and then diminished.

E. G.

**Conductivity and Dissociation of Organic Acids in Aqueous Solution at Different Temperatures.** GEORGE F. WHITE and HARRY C. JONES (*Amer. Chem. J.*, 1910, 44, 159—199).—In a preliminary paper (this vol., ii, 13), an account was given of the conductivity of several organic acids at temperatures between 0° and 35°. The work has now been extended to many other acids, and complete data are given for the conductivity and dissociation of all the acids examined. The conclusions arrived at previously are confirmed.

It is not possible to make any general statement with regard to the change in dissociation of the organic acids with change of temperature. With many of the acids, namely, acetic, propionic, phenylacetic, hippuric, malonic, maleic, fumaric, crotonic, benzoic, *m*-toluic, cinnamic, salicylic, and *m*-hydroxybenzoic acids, a maximum dissociation occurs between 25° and 35°. With other acids, namely, succinic, itaconic, racemic, methylsuccinic, citric, *p*-hydroxybenzoic, gallic, aniline-*m*- and *p*-sulphonic, and *o*- and *p*-aminobenzoic acids, the dissociation increases from 0° to 35° without a maximum, but several of these give indications that a maximum would appear at a slightly higher temperature. The dissociation of *n*- and *iso*-butyric, mandelic, citraconic, mesaconic, *o*-toluic, and *o*-phthalic acids decreases regularly with rise of temperature from 0°. It is therefore obvious that isomeric acids do not behave similarly with respect to change in dissociation. The migration velocities of isomeric ions are identical. The dissociation of the organic acids in relation to temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants, and, since maxima in dissociation occur with many of the acids, it is evident that some other force or forces must be exerted in such cases.

E. G.

**Electrical Resistance of the Alkali Metals.** L. HACKSPILL (*Compt. rend.*, 1910, 151, 305—308).—The specific resistances of sodium, potassium, rubidium, and caesium at different temperatures are recorded, and the results, except in the case of sodium, shown to be considerably lower than those obtained by Guntz and Broniewski (*Abstr.*, 1909, ii, 113). The determinations were made in tubes completely filled with the metal in order to avoid the presence of the inert gases employed by Guntz and Broniewski.

W. O. W.

**Simple Relation between the Size of the Atoms of Metals and the Temperature-coefficient of the Resistance.** FRANZ STREINTZ (*Ann. Physik*, 1910, [iv], 33, 436—440).—It is shown that for certain series of metals the cube-root of the atomic volume is proportional to the temperature-coefficient of the electrical resistance between 18° and 100°. Palladium, platinum, aluminium, silver, gold, cadmium, and tin form such a series, and the data for zinc, lithium,

and mercury indicate that the proportionality factor has approximately the same value as for the metals of this series. The proportionality factor is, however, to some extent dependent on the atomic volume of the metal, being greater for metals of atomic volume less than 8.9 and smaller when the atomic volume exceeds 16.3. This variation is considered with reference to the data for lead, bismuth, thallium, sodium, potassium, copper, iron, nickel, glucinum, and cesium. H. M. D.

**Hydration and Molecular Heat of Ions in Very Dilute Aqueous Solutions.** GUSTAV MIX (*Ann. Physik*, 1910, [iv], 33, 381—399).—A theoretical paper in which the equilibrium between the undissociated molecules and the ions of an electrolyte is examined from a kinetic point of view. The free ions are supposed to undergo hydration in stages, and this process requires a certain time which is comparable with the average period during which the ions exist as such in the aqueous solution before re-combination takes place. Since the average life of the ions diminishes as the concentration of the electrolyte increases, it follows that the ions are less hydrated in concentrated than in dilute solutions. In very dilute solutions the average hydration of the ions reaches a constant maximum value, and it is shown that for such solutions the rate of re-combination of the ions can be calculated by means of Langevin's formula.

The free energy of the ionisation process and the coefficient of ionisation are shown to be dependent on the degree of hydration, and these relationships are considered with reference to experimental data for solutions of potassium chloride and acetic acid. H. M. D.

**Chemical Actions and Ionisation.** G. REBOUL (*Compt. rend.*, 1910, 151, 311—312. Compare Abstr., 1909, ii, 718; Broglie and Brizard, Abstr., 1909, ii, 535, 637).—The author has repeated the experiments on the oxidation of sodium and the interaction of ammonia and hydrogen chloride, recently called into question by Broglie and Brizard (this vol., ii, 11), and maintains the accuracy of his observations. When nitric oxide and oxygen are allowed to combine in the apparatus already described, no electrical charge is developed if the apparatus is constructed of platinum, whereas when it is made of copper or brass, a charge is produced, probably through the action of the gas on the electrodes. W. O. W.

**Electro-capillary Phenomena with Fused Salts.** G. v. HEVEY and RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1910, 74, 443—465).—The arrangement of the apparatus, which was used for temperatures up to 800°, corresponded with that of the ordinary capillary electrometer; the electrodes were of graphite, and the glass capillary was about 1 mm. in diameter and 10 cms. long.

The system made up of fused lead in contact with fused lead chloride showed no electro-capillary phenomena. The following systems, however, gave results closely resembling those obtained with the ordinary mercury-sulphuric acid electrometer:  $\text{Pb} | \text{KCl}$ ;  $\text{Pb} | \text{KI}, \text{KCl}$ ;  $\text{Pb} | \text{NaI}, \text{NaCl}$ ;  $\text{Sn} | \text{LiCl}, \text{KCl}$ ;  $\text{Hg} | \text{LiNO}_3, \text{KNO}_3$ . The curves were of parabolic form in each case, but the relative extent of the

rising and falling branches varied considerably. The position of the maxima of the curves when lead was used with different electrolytes only varied between 1.36 and 1.44 volts, although the temperatures differed by as much as 200°.

The sensitiveness of these electrometers is only about 1/1000 that of the ordinary capillary electrometer. The following systems:  $\text{Hg} \mid \text{BaI}_2$  in pyridine, and  $\text{Hg} \mid \text{KCl}$  in fused antimony trichloride, are of the same order of sensitiveness as those made up with fused salts.

The effect of the addition of lead chloride to fused potassium chloride in the system  $\text{Hg} \mid \text{KCl}$  has been measured, and from the results the equilibrium concentration of lead chloride in the system  $\text{Pb} + 2\text{KCl} \rightleftharpoons \text{PbCl}_2 + 2\text{K}$  has been calculated.

The above results are shown to be qualitatively in complete accord with the accepted theory of electro-capillary phenomena

G. S.

**Arc Characteristics in Gases and Vapours.** MASAMICHI KIMURA and KIYOSHI YAMAMOTO (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 47—58).—The connexion between the voltage, current, and the length of arc which could be maintained between a carbon cathode and a water-cooled copper anode surrounded by various gases and vapours has been determined. The gases and vapours used were hydrogen, hydrogen mixed with benzene, methyl alcohol, a mixture of methyl alcohol and ethyl alcohol (composition not stated), ethyl alcohol, and air. For a given current and a given length of arc, the arc in an atmosphere of hydrogen, or of hydrogen mixed with benzene vapour, requires a larger voltage than in the case of the other vapours and of air. The gases and vapours mentioned above are arranged in the order of their relative efficiency for the production of undamped electrical oscillations.

T. S. P.

**Compressibilities of Helium and Neon.** FRANK P. BURT (*Trans. Faraday Soc.*, 1910, 6, 19—25).—The apparatus described by Gray and Burt (*Trans.*, 1910, 95, 1659) has been used to obtain the pressure-volume isothermals of helium and neon at 0°.

In the case of helium,  $pv$  is constant from 838 mm. to 147 mm. pressure. With neon the value of  $pv$  varies from 58.944 at 860 mm. to 58.886 at 144 mm. A tendency in the values at low pressures to be abnormally high with both gases is attributed to a constant error in the apparatus.

A straight line isothermal could be drawn between the twenty-one values of  $pv$  for neon obtained by smoothing the experimental values. The compressibility coefficient of neon between 0 and 1 atm. pressure is +0.00105, that is, neon, like hydrogen, is an ultraperfect gas. The compressibility coefficient of helium between the limits of pressure studied is zero. Helium behaves like a gas with a much higher critical temperature than it really possesses.

R. J. C.

**Compressibility Coefficients of Liquids.** W. A. SUCHODSKI (*Zeitsch. physikal. Chem.*, 1910, 74, 257—276).—A modified form of

the Oersted-Röntgen compressibility apparatus, so designed that it can conveniently be kept at any desired constant temperature, is described. With this apparatus the compressibilities,  $\beta$ , at comparatively low pressures of a number of pure liquids at temperatures in the neighbourhood of  $14^\circ$ ,  $35^\circ$ , and (in some cases)  $100^\circ$  have been determined. The values of  $\beta \times 10^6$ , corrected for the compression of the glass, are as follows: Ethyl bromide, 113.4 at  $13.7^\circ$ , 138.4 at  $35^\circ$ ; ethyl ether, 163.0 at  $12.2^\circ$ , 206.9 at  $34.8^\circ$ ; amylene, 170.5 at  $16.7^\circ$ , 209.2 at  $34.7^\circ$ ; benzene, 86.8 at  $12.9^\circ$ , 100.3 at  $34.9^\circ$ , and 189.8 at  $99.9^\circ$ ; fluorobenzene, 87.7 at  $13.9^\circ$ , 102.6 at  $35.3^\circ$ , and 189.8 at  $99.7^\circ$ ; chlorobenzene, 67.1 at  $13.3^\circ$ , 77.0 at  $35.4^\circ$ , and 127.4 at  $100.4^\circ$ .

The formula  $\beta = 0.0006V/T$ , in which the symbols have the usual significance and apply for the boiling point in each case, is deduced by means of certain approximations from van der Waals' equation, and admits of the calculation of  $\beta$  at the boiling point of the liquid in question, both from density determinations and from the volume measurements of Kopp. It is shown that the observed and calculated values of  $\beta$  for non-associated liquids are in fair agreement. G. S.

**Thermal Expansion of Metals.** EDUARD GRÜNEISEN (*Ann. Physik*, 1910, [iv], 33, 33—64. Compare Abstr., 1908, ii, 563).—The dependence of the thermal expansion of various metals on the temperature has been examined. The data of previous observers were made use of in the case of platinum, palladium, copper, silver, aluminium, iron, nickel, and iridium. For magnesium, zinc, cadmium, antimony, iridium, gold, lead, and bismuth, new measurements of the linear expansion between  $-183^\circ$  and  $+100^\circ$  have been made. It is found that the observed expansion is, in general, in close agreement with that required by Thiesen's exponential formula,  $l_2 - l_1 = \gamma(T_2^{1+\epsilon} - T_1^{1+\epsilon})$ , and this agreement is particularly good at low temperatures. Zinc, cadmium, and tin are, however, exceptions, and the abnormal behaviour in these cases is supposed to be due to discontinuous changes in the structure of the metals.

The experimental data do not indicate whether the above formula can be employed for extrapolation to temperatures in the neighbourhood of absolute zero. They show, however, that the exponent  $\epsilon$  is a periodic function of the atomic weight of the metal, and that its maximum values are reached when the atomic volumes are at their respective minima. H. M. D.

**Influence of Temperature and Pressure on the Coefficient of Expansion and the Specific Heat of Metals.** EDUARD GRÜNEISEN (*Ann. Physik*, 1910, [iv], 33, 65—78. Compare previous abstract).—From a comparison of the mean coefficients of expansion and the mean specific heats of the metals enumerated in the previous paper for the two temperature intervals  $-190^\circ$  to  $17^\circ$  and  $17^\circ$  to  $100^\circ$ , the author finds that the influence of temperature is the same in the two cases. Within the limits of experimental error the ratio of the expansion coefficient to the specific heat is independent of the temperature. It follows from this that the variation of the specific heat with the temperature can be represented by Thiesen's exponential formula.

From measurements of the compressibility of aluminium, iron, copper, silver, and platinum at different temperatures, it is found that the relative changes of the density and of the specific heat, which are brought about by a given change of pressure, are of the same order of magnitude.

H. M. D.

**Use of Cooling Curves in Determining the Cryoscopic Point of Solution.** M. MOULIN (*J. Chim. Phys.*, 1910, 8, 321—330).—When a dilute solution, losing heat energy at a constant rate by cooling, becomes supercooled, the separation of a particle of solid causes an abrupt rise in temperature to the freezing point. Since, however, a certain amount of solid is deposited in this process, the temperature observed is rather lower than the true freezing point of the original solution. The cooling curve presents a rapid fall during the liquid phase, a sudden rise to a maximum from the super-solubility point, followed by a gradual fall during separation of the solid. When the last part of the curve is extrapolated to cut the first part, the true freezing point is found. The experimental maximum is not sharply defined, owing to lag in the thermometer readings, but this lag does not affect the accuracy of the freezing-point values.

Cooling-curve determinations of molecular weight have been made with  $\epsilon$ -rhamide, sugar, and resorcinol in water, naphthalene in benzene, and water in acetic acid.

R. J. C.

**Impossibility of Superheating a Solid.** A. BERTHOUD (*J. Chim. Phys.*, 1910, 8, 337—339).—It is possible to supercool a clear liquid because the very minute crystal nuclei which tend to form possess a surface energy greater than massive crystals and redissolve. If a drop of the liquid phase is placed on a solid at its melting point, it wets the surface and tends to spread as far as possible over it. Hence the solid has its surface energy diminished by contact with its liquid, and is thereby predisposed to melt rather than become superheated. Superheating would only be possible with a solid which on melting gave a liquid which did not wet its surface.

Sodium chloride hydrate,  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ , which usually decomposes at  $-12^\circ$ , was heated to  $+15^\circ$  by Frankenheim (1861), but this is a case of arrested decomposition, as the true melting point of the hydrate is probably  $+15^\circ$  or above.

R. J. C.

**Freezing-point Curves of Gaseous Mixtures: Compounds of Methyl Ether and Methyl Alcohol with Ammonia.** GEORGES BAUME and F. LOUIS PERROT (*Compt. rend.*, 1910, 151, 523—530; Compare Abstr., 1909, ii, 545).—The freezing-point curve for the system methyl alcohol-ammonia shows a well-defined maximum corresponding with the compound  $\text{MeOH} \cdot \text{NH}_3$ . The curve for mixtures having 80—95% of alcohol could not be investigated, owing to the existence of uncrystallisable glasses. The curve for methyl ether-ammonia has a maximum corresponding with the formula  $\text{OMe} \cdot \text{NH}_3$ , but this is not well defined owing to dissociation.

W. O. W.

**Application of Thermal Analysis to Several Binary Organic Systems.** DEMETRIUS E. TSAKALOTOS and PHILIPPE A. GUYE (*J. Chim. Phys.*, 1910, 8, 340—357. Compare Wroczynski and Guye, this vol., ii, 699).—The liquidus curves of the following mixtures are normal, and show no sign of additive compounds: phenol + benzene, benzene + thiophen, nitrobenzene + ethyl ether, aniline + chloroform. Benzene and thiophen form no eutectic, the freezing-point curve being characteristic of isomorphous mixtures. Freezing-point determinations were not possible with mixtures of phenol and benzoyl chloride, owing to the production of hydrogen chloride even at low temperatures. For a similar reason mixtures of bromine with benzene could not be studied.

Trichloroacetic acid with ethyl ether and acetone with chloroform give mixtures so viscous that freezing-point determinations are impracticable. The system acetone + chloroform in the presence of potassium hydroxide gives an additive product melting at 97°, namely,  $\text{CMe}_2\text{OH}\cdot\text{CCl}_3$ . On mixing the components without alkali an appreciable amount of heat is liberated. This evidence and also the high viscoelastic point to the formation of an additive compound (compare Tsakalotos, Abstr., 1908, ii, 260).

The high viscosity of ethyl ether with trichloroacetic acid is held to indicate the formation of an additive compound in which the ether functions as a basic substance. The mixture with 69% of acid sets to an isotropic mass at  $-60^\circ$ . Mixtures of aniline and ethyl acetate behave in a similar way (this vol., ii, 699).

The authors have determined the freezing-point of purified ethyl ether to be  $-112.1^\circ$ , a value in agreement with that given by Ladenburg and Krügel ( $-112.6^\circ$ ), but not with that of Olszewski ( $-117.4^\circ$ ) or Guttman ( $-117.6^\circ$ ). R. J. C.

**Cryoscopy of the Naphthylamines and their Additive Compounds.** ABEL BUGUET (*Compt. rend.*, 1910, 151, 312—313).—The freezing-point curve for mixtures of chloro-2:4-dinitrobenzene shows two minima and a single maximum, the latter corresponding with the existence of the hydrochloride of 2:4-dinitrophenyl- $\alpha$ -naphthylamine. This has also been obtained in large, garnet-red crystals, m. p.  $69^\circ$ , by mixing the constituents in anhydrous solvents. The hydrochloride of 2:4-dinitrophenyl- $\beta$ -naphthylamine has m. p.  $65^\circ$ . Mixtures of these salts with naphthalene give freezing-point curves having minima at  $51.5^\circ$  and  $73^\circ$  respectively. *m*-Dinitrobenzene gives W-shaped curves with  $\alpha$ - and  $\beta$ -naphthylamine, and in each case garnet-red crystals of additive compounds were isolated, having m. p.  $60$ — $63^\circ$  and  $57^\circ$  respectively. W. O. W.

**Thermodynamic Calculation of the Vapour Pressure of Water and Ice.** WALTHER NERNST (*Ber. Deut. physikal. Ges.*, 1910, 12, 565—571).—The value recently obtained by Scheel and Heuse (*Ann. Physik*, 1910, [iv], 31, 715) for the vapour pressure of water at  $50^\circ$  has been employed to recalculate the constants in the thermodynamic equation for the vapour pressure of water. The vapour-pressure values calculated from the new equation are in almost complete agreement with the measured values for temperatures

between  $0^{\circ}$  and  $50^{\circ}$ ; considerably greater differences are found between  $50^{\circ}$  and  $100^{\circ}$ .

The recent determinations of the specific heat of ice between  $-10^{\circ}$  and  $-200^{\circ}$  are also utilised in the determination of the constants involved in the thermodynamic equation for the vapour pressure of ice. Calculated and observed pressures are shown to be in satisfactory agreement.

H. M. D.

**Relations between the Properties of Liquids at the Boiling Point.** DAN TYRER (*Phil. Mag.*, 1910, [vi], 20, 522—533).—An empirical relationship connecting the latent heat of vaporisation and the molecular volume of a liquid at its boiling point has been found to hold for a large number of organic compounds. This is expressed by  $LM = K\sqrt{V}$ , in which  $L$  is the latent heat,  $M$  the molecular weight,  $V$  the molecular volume, and  $K$  a constant. By taking  $K = 1583$ , it is shown that the calculated heats of vaporisation are in good agreement with those found by experiment. The only classes of substances which do not seem to conform to this relationship are the aliphatic hydrocarbons and ethers, and also associated liquids. For associated liquids which do not dissociate on vaporisation the calculated latent heats are greater than the observed values. On the other hand, for associated liquids which dissociate on vaporisation, the calculated heat values are greater or smaller than those found by experiment according to the magnitude of the heat of dissociation.

By combining the above relationship with Trouton's rule, the molecular volume and the boiling temperature are shown to be connected by the equation  $T = K_1\sqrt{V}$ . For the various members of a homologous series, an approximately constant value of  $K_1$  is obtained, but this value varies appreciably from one series to another. For aliphatic hydrocarbons and ethers,  $K_1 = 68$ ; for aliphatic chlorides and amines,  $K_1 = 70$ ; for aliphatic esters and bromides,  $K_1 = 74$ ; for aliphatic iodides and aromatic hydrocarbons,  $K_1 = 79$ , and for aromatic ethers,  $K_1 = 83$ . The relationship is also affected by molecular association, the value of  $K_1$  being much greater for associated than for normal liquids.

H. M. D.

**Determination of Boiling Point. I. Fall of Temperature in Vapours of High Molecular Complexity at Small Pressures.** CHRISTIAN J. HANSEN (*Zeitsch. physikal. Chem.*, 1910, 74, 65—114. Compare *Abstr.*, 1909, ii, 212, 969).—An apparatus suitable for the investigation of the distillation of compounds of high boiling point under the pressure of their own vapour is figured and described in detail. The liquid to be distilled was heated electrically when necessary, and the distillation vessel provided with a jacketing arrangement, by means of which it could be heated from the outside to any desired temperature. One of the main objects of the investigation was to measure the variation of temperature along the column of vapour. This was at first effected by thermometers placed at different levels in the tube, and in the final form of apparatus by a thermocouple which could be moved up and down in the vapour.

Experiments were made with palmitic, stearic, myristic, and lauric



acids under the most varying conditions, and the results are described in detail. Under certain conditions it makes comparatively little difference whether the distillation flask is jacketed or not. The experiments with the thermocouple show clearly that the temperature gradually rises as the couple is progressively raised in the column of vapour. The effect of different degrees of internal heating is fully discussed. It was found that there is a great tendency for the solutions to become superheated. Some experiments were made with palmitic acid without internal heating, and in these experiments the difference in temperature between the upper and lower thermometers was remarkably constant, amounting to about  $0.4^{\circ}$  per cm.

A method proposed by von Rechenberg, according to which the distilling flask is completely immersed in a bath, did not lead to satisfactory results.

G. S.

**Heat of Formation of the Oxides of Cobalt and Nickel and the Heat of Combination of Acidic Oxides with Sodium Oxide.** WILLIAM G. MIXTER (*Amer. J. Sci.*, 1910, [iv], 30, 193—201. Compare this vol., ii, 585).—The quantities of heat liberated in the oxidation of cobalt, nickel, zinc, and manganese, and certain of the lower oxides of these metals, have been measured. From the experimental data the following thermal values are derived:  $\text{Co} + \text{O} = \text{CoO}$  (crystalline)  $+ 57.5$  cal.;  $\text{Co} + \text{O} = \text{CoO}$  (amorphous)  $+ 59.5$  cal.;  $3\text{Co} + 4\text{O} = \text{Co}_3\text{O}_4 + 193.4$  cal.;  $\text{Co} + 2\text{O} + \text{Na}_2\text{O} = \text{Na}_2\text{CoO}_3 + 100.2$  cal.;  $\text{Zn} + \text{O} + \text{Na}_2\text{O} = \text{Na}_2\text{ZnO}_2 + 87.0$  cal.;  $\text{Mn} + 3\text{O} + \text{Na}_2\text{O} = \text{Na}_2\text{MnO}_3 + 169.0$  cal., and  $\text{MnO}_2 + \text{O} + \text{Na}_2\text{O} = \text{Na}_2\text{MnO}_4 + 49.4$  cal. The oxidation of nickel by means of sodium peroxide is very incomplete, and the thermal data are considered to be somewhat untrustworthy. The actual results seem to show, however, that the heat of formation of the oxide is practically the same as in the case of cobalt:  $\text{Ni} + \text{O} = \text{NiO} + 57.9$  cal.

H. M. D.

**Heat of Combustion of Some Hydronaphthalene Derivatives.** HENRI LEROUX (*Compt. rend.*, 1910, 151, 384—387).—The following results have been obtained for the heats of combustion of liquid naphthalene and its products of hydrogenation: naphthalene,  $-19$  Cal. (solid,  $-14.6$  Cal.); dihydronaphthalene,  $-25$  Cal.; tetrahydronaphthalene,  $4$  Cal.; hexahydronaphthalene,  $6$  Cal.; octahydronaphthalene,  $33$  Cal., and naphthane,  $61$  Cal. These values are in accordance with the facts already known in connexion with the hydrogenation of naphthalene, and in the author's opinion are best explained by Bamberger's formula for this hydrocarbon.

W. O. W.

**Heat of Hydration. III.** WILLEM P. JORISSEN (*Chem. Weekblad*, 1910, 7, 761—768. Compare this vol., ii, 269).—An application of the author's method of determining heat of hydration to zinc sulphate, manganese sulphate, magnesium sulphate, sodium phosphate, sodium carbonate, and strontium chloride, and a comparison of the values obtained with those given by Thomsen

A. J. W.

**Variations of the Physical Properties of Metallic Alloys Subjected to Mechanical and Thermal Action. I. Specific Gravity.** R. PANNAIN (*Gazzetta*, 1910, 40, i, 431—433).—The experiments were carried out with coinage bronze (about 4% tin) and silver (16.5% copper), and they show that a marked increase in specific gravity is produced by hammering, the increase being maintained or, rather, increased after a subsequent annealing. Bronze of D 8.76965 after being annealed and hammered (alternately) three times, and coined, had D 8.94623. Coinage silver of D 9.99932 had D 10.21636 after a similar treatment. R. V. S.

**The Rectilinear Diameter for Oxygen.** ÉMILE MATHIAS and HEIKE KAMERLINGH ONNES (*Compt. rend.*, 1910, 151, 474—475. Compare this vol., ii, 771).—This paper contains the summarised numerical results of the determinations outlined in a previous communication. It is shown that the diametral line for oxygen is very nearly rectilinear. The densities of liquid oxygen at low temperatures are not in agreement with those of Dewar (1893) or of Baly and Donnan (*Trans.*, 1902, 81, 911). W. O. W.

**Nature of the Transition Layer between Two Adjacent Phases.** WILLIAM C. MCC. LEWIS (*Phil. Mag.*, 1910, [vi], 20, 502—511).—The values obtained for the internal pressure of a liquid differ considerably according to whether these are calculated from van der Waals' equation or from the work required to remove unit volume from the surface layer of the liquid outside the range of molecular attraction. This divergence is supposed to be due to the average density in the surface layer being greater than the ordinary bulk density.

From Bakker's equation for the latent heat of vaporisation, the relationship  $\lambda_i = a/v_s$  is deduced, in which  $\lambda_i$  is the internal heat of vaporisation,  $a$  the van der Waals' constant, and  $v_s$  the average volume of one gram of the substance in the surface layer. From this relationship the average surface densities of sixteen liquids are calculated for their respective boiling points. The values thus obtained are approximately 2.5 times the bulk densities of the liquids.

In the case of water, the surface density has been calculated for temperatures between 0° and 100°. As the temperature rises the densities converge somewhat, the ratio falling from 2.189 at 3.6° to 2.023 at 100°. The temperature variations of the internal pressure, both in the bulk and in the surface layer, are also tabulated.

The change in the density of water, which is involved in its transition from the bulk of the liquid to the surface layer, is accompanied by a heat effect which is calculated to be 0.0034 cal. per unit area of surface. This is of the same order as the heat effect found by Parks on moistening powders with water. H. M. D.

**Variation with Temperature of Viscosities of Gases of the Argon Group.** A. O. RANKINE (*Proc. Roy. Soc.*, 1910, A, 84, 181—192. Compare this vol., ii, 409).—In comparing gaseous

viscosities at  $100^{\circ}$  with those at room temperature, a correction  $(1 - 2\gamma\theta)$  is necessary, where  $\gamma$  is the coefficient of linear expansion of the glass capillary tube, and  $\theta$  the temperature interval. The correction due to alteration of the mean free path of the molecules is negligible, but a small unknown error is introduced by the alteration in surface tension of the mercury pellet which constitutes the driving piston.

The viscosity of air and the argon gases increases by about 20–25% when the temperature is raised to  $100^{\circ}$ . Assuming that the increase follows a linear law,  $\eta_{\theta} = \eta_0(1 + \beta\theta)$ , where  $\eta_{\theta}$  is the viscosity at temperature  $\theta$ , the values of the temperature-coefficient,  $\beta \times 10^5$ , are: air, 266; helium, 232; neon, 221; argon, 283; krypton, 308; xenon, 339. The actual viscosities at  $0^{\circ}$ ,  $\eta_0 \times 10^4$ , are: air, 1.879; neon, 2.081; argon, 2.102; krypton, 2.334; xenon, 2.107. The temperature-coefficients of viscosity are not proportional to the viscosities.

According to Sutherland the temperature-coefficient of gaseous viscosity is  $\sqrt{T}(1 + C/T)$ , where  $T$  is the absolute temperature and  $C$  a constant depending on the attraction between the molecules of the gas. The values of  $C$  calculated by the author are: air, 116; helium, 70; neon, 56; argon, 142; krypton, 188; xenon, 252. Certain of these are in fair accord with values obtained by Rayleigh and by Schultze. A simple ratio, about 1.14, exists between  $C$  and the critical temperature in the case of argon, krypton, xenon, nitrogen, oxygen, carbon dioxide, ethylene, and nitrous oxide. With helium and hydrogen, the value of  $C$  is much higher than this relation indicates, although for a perfect gas  $C$  should be zero.

The mutual attraction between the molecules,  $C$ , which has the effect of making collisions more frequent may be expressed in terms of an increase in cross sectional area of the molecule,  $1:(1 + C/T)$ . The author calculates the molecular volume and molecular density of the argon group relative to helium. The size and density of the atoms apparently increase with increase in atomic weight. R. J. C.

**The Internal Friction of Albumin Solutions.** W. PAULI and R. WAGNER (*Biochem. Zeitsch.*, 1910, 27, 296–303).—The internal friction of serum albumin solutions in the presence of varying quantities of hydrochloric acid was determined, and found to attain a maximum when the latter was 0.02*N* and when the concentration of the protein was 1.7%. This shows a deviation for the number obtained by Michaelis and Mostynski (this vol., ii, 592). The authors criticise the investigations of Michaelis on the determination of the isoelectric point of proteins, and maintain that the solutions employed were not sufficiently pure, that the globulins had been separated by half-saturation with ammonium sulphate, and that the solution containing the albumin had not been dialysed for a sufficient length of time, and contained a certain amount of combined ammonia, showing therefore the isoelectric point in the presence of a higher concentration of acid. S. B. S.

**Anomalous Adsorption.** WILHELM BILTZ and HANS STEINER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 113–122).—It is found that

the adsorption of night-blue by cotton wool increases at first with the concentration of the solution and then decreases in more highly concentrated solutions of the colouring matter. This behaviour is not in accordance with the exponential adsorption formula, and is regarded as an example of anomalous adsorption. The relationships are essentially the same whether technical or dialysed night-blue is used in the experiments; they are qualitatively the same whether the absorption takes place at the ordinary temperature or in boiling solutions. Similar effects have also been observed in the adsorption of night-blue by animal charcoal and of victoria-blue and Congo-red by cotton wool, and it is pointed out that like deviations from the exponential formula have also been found in the adsorption of copper sulphate by clay and of agglutinin by bacteria.

In the case of night-blue, victoria-blue, and copper sulphate, the observed effects are supposed to be due to hydrolysis of the substance in solution, the hydrolysed base being adsorbed. The relatively large amount of adsorption in dilute solution is attributed to the increased hydrolysis, and the effect of temperature in reducing the degree of abnormality is shown to be consistent with this hypothesis. Observations relating to the adsorption of benzopurpurine, alizarinecyanine green-G extra, and acid-alizarin-blue are also recorded which show that in these cases the adsorption is more or less normal.

H. M. D.

**Thermal Dissociation of Calcium Carbonate.** \*JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1910, 32, 938—946).—The work of previous authors on the equilibrium pressure of the reaction  $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$  has been rendered somewhat inaccurate by a lack of definiteness in the temperature of the reacting system. In the present investigation this error has been obviated by using a very small quantity (0.1 gram) of material, so that the extreme variation throughout the charge did not exceed 2°. The apparatus employed and the mode of determining the temperature are described.

The results of four series of measurements are expressed by the equation  $\log p = (-9340/T) + 1.1 \log T - 0.0012T + 8.882$ , where  $p$  is the equilibrium pressure in mm. of mercury at the absolute temperature  $T$ . This equation represents the results much better than Riesenfeld's formula (this vol., ii, 126).

E. G.

**Thermodynamics of the Capillary Layer of a Pure Substance between the Homogeneous Liquid and Vapour Phases.** GERBET BAKKER (*Zeitsch. physikal. Chem.*; 1910, 73, 641—666. Compare Abstr., 1907, ii, 434).—A mathematical paper. Equations are deduced which give the relationships between the different factors determining the nature of the capillary layer separating the vapour and liquid phases of a pure substance for different degrees of curvature of that layer. An expression is deduced for the internal heat of evaporation, and it is shown that when the capillary layer becomes flat (that is, of infinite radius) the expression reduces to the well-known Clapeyron-Clausius equation. Another equation gives the mean thickness of a cylindrical capillary layer in terms of the curvature,

surface tension, and other factors concerned, and it is shown that when the radius of the layer is infinite, liquid and vapour contribute to the capillary layer in quantities proportional to their densities. When the law of Cailliet and Mathias (law of the rectilinear diameter) holds, the mean thickness of a flat capillary layer is a diminishing linear function of the temperature.

G. S.

**Surface Tensions of Some Unsaturated Organic Compounds.** FREDERICK H. GETMAN (*Amer. Chem. J.*, 1910, 44, 145—158).—On account of the value of surface-tension measurements for the determination of molecular complexity, the author is carrying out a systematic investigation of the surface tension of a series of closely related unsaturated organic compounds. The present paper deals with mesityl oxide,  $\beta$ -dimethylacrylic acid, styryl methyl ketone, styryl ethyl ketone, and benzylidenepinacolin. The measurements were made by the capillary method, the apparatus employed being a modification of that used by Przyluska (this vol., i, 106).

The results are arranged in tables, which record the observed capillary elevation, the density, the surface tension, and the coefficients of variation of molecular surface tension at various temperatures. Curves have been constructed in which the surface tensions are plotted as ordinates and the temperatures as abscissae. All the substances examined, except dimethylacrylic acid, have been found to be non-associated. The values of  $n$  (the number of atoms in the molecule) obtained by this method agree closely with those calculated by means of Longinescu's formulae (*Abstr.*, 1903, ii, 531) correlating the number of atoms in the molecule of a substance with the absolute boiling or melting point and the density. The average values of the coefficient  $k$  in Ramsay and Shields' formula for the non-associated compounds are in all cases greater than 2.12, the mean value assigned by Ramsay and Shields. The association of  $\beta$ -dimethylacrylic acid decreases slowly with increase of temperature. E. G.

**Studies of the Processes Operative in Solutions. XI. The Displacement of Salts from Solution by Various Precipitants.** HENRY E. ARMSTRONG and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1910, A, 84, 123—136. Compare *Abstr.*, 1907, ii, 848).—Previous measurements of the precipitating influence of ethyl alcohol and hydrogen chloride on various salts have been repeated, and the study has been extended to methyl and propyl alcohols, dextrose, etc. The new determinations made at 25° and 0° reveal small errors in the previous work, but do not affect the general conclusions.

Particular care was taken to obtain pure salts, which were centrifuged to remove occluded mother liquors, and graded to obtain particles of uniform size and remove fine powder. Slight differences in solubility between different samples of the same salt render it necessary to compare each solubility in presence of a precipitant with the original solubility of the same sample of salt.

As before, the effect of precipitants is calculated as if it were a simple dehydrating one and expressed as "apparent molecular hydration" of the precipitant. The value obtained denotes the amount

of water thrown out of action as solvent water without postulating any particular mechanism by which the precipitant acts.

The action of the non-electrolytes, methyl alcohol, ethyl alcohol, and propyl alcohol, is exactly comparable with that of hydrogen chloride, although less intense. Of the three alcohols, methyl is the least and propyl the most active precipitant. Of the chlorides, ammonium chloride is least and potassium chloride most affected. Sodium chloride occupies an intermediate position, and exhibits the peculiarity that at 0° small amounts of precipitant produce less effect than at 25°. In all other cases the precipitants are more active at 0° than at 25°. Although the superior effect produced by hydrogen chloride must be attributed to a direct dehydrating action, the precipitants do not act merely by attracting water. Methyl alcohol, which is the more soluble and presumably more hydrated, is not so active a precipitant as propyl alcohol. The effect of the precipitant is to increase the proportion of hydrone ( $H_2O$ ) and the other simpler molecules present in water, which in virtue of their tendency to polymerise and form water condition the dehydration of the hydrated solute molecules. The greater effectiveness of the precipitant at 0° may be due to the greater complexity of the water, giving more opportunity for the precipitant to depolymerise it; also to the larger proportion of complex, easily precipitated, salt molecules.

The reduction of molecular conductivity of the salts by the three alcohols is exactly parallel to the reduction in solubility. In all cases the effect is greater at 0° than at 25°. Increased solubility is noticed with potassium chloride in presence of potassium nitrate and potassium and sodium chlorides in presence of dextrose. In the latter case a compound of salt with sugar is held responsible, whereas in the former it is supposed that the nitrate has a depolymerising effect on the chloride. Potassium chloride acts as a precipitant of the nitrate. In general, the nitrates are more easily precipitated than chlorides, in accordance with the view that nitrates have less affinity for water than chlorides.

The precipitation of salts from solution is mainly due to dehydration changes, conditioned not only by the direct removal of water from the solution by the precipitant, but also, in the case of neutral precipitants particularly, by the agency of the increased proportion of hydrone molecules produced in the water by the mechanical interposition of the molecules of the precipitant.

R. J. C.

Is the Iron-Nickel Meteorite Stable or Metastable? W. GUERTLER (*Zeitsch. physikal. Chem.*, 1910, 74, 428-442).—Fraenkel and Tammann (Abstr., 1909, ii, 157) have brought forward evidence to show that meteoric iron-nickel is unstable, but the author attempts to show from the available data that this is not the case. The different structure of the meteoric alloy is ascribed to the action of a force tending to draw similar constituents together, corresponding with the tendency of small crystals in contact with a saturated solution to pass into larger crystals. It is shown that the formation of the characteristic meteoric structure can occur only at low temperatures, and as the "collective crystallisation" process is extremely slow under such con-

ditions, it can only be fairly complete when unlimited time is available, as in the case of a meteorite. G. S.

**Transformation of Amorphous into Crystalline Substances.** CORNELIO DOELTER (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 88—92. Compare this vol., ii, 696).—In reference to the view that the "amorphous" and crystalline forms of a substance are not essentially different, the author discusses the influence of the size of the particles on the physical properties. Experiments are described which show that slightly soluble mineral substances, which have been precipitated in "amorphous" form, can be readily converted into a definite crystalline form by shaking with water for considerable periods of time. The same effect is produced without shaking if the amorphous substances are heated in contact with water at 60—70°. H. M. D.

**Crystallisation from Aqueous Solutions. IV.** ROBERT MARC (*Zeitsch. physikal. Chem.*, 1910, 73, 685—723. Compare Abstr., 1908, ii, 160; 1909, ii, 798, 983).—Many of the experiments described in the previous papers have been repeated by more accurate methods, and the majority of the earlier results are confirmed. The conductivity method of following the results has proved to be inaccurate, more particularly in the early stages of the reaction, and in the present series of experiments the concentrations have mostly been determined by direct analysis.

The reaction is of the second order only up to 13°; above that temperature the speed of crystallisation is simply proportional to the supersaturation of the solution.

Further evidence is adduced that the retarding effect of dyes is connected with adsorption. It is shown that the dyes retard crystallisation proportionally to the extent to which they are adsorbed, and, further, they act by diminishing the active mass in the surface layer. In the presence of dyes, the solutions approach an apparent point of equilibrium with the same velocity constant as they approach the true equilibrium point in the absence of dyes.

The results are not sufficiently accurate to admit of the establishment of a relationship between concentration and amount adsorbed. The rate of crystallisation in the presence of dyes is also of the first order at relatively high temperatures. G. S.

**Classification of Disperse Systems.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 155—157).—A modification of Ostwald's classification of the various types of colloidal solutions is suggested. H. M. D.

**Examples of Compound Disperse Systems.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 157—158).—When concentrated solutions of the thiocyanates of the alkaline earth metals are mixed with a concentrated solution of manganese sulphate, the alkaline earth sulphates are precipitated in a colloidal (gelatinous) form having a cellular structure. If the containing vessels are rapidly cooled in liquid air, the intercellular solution solidifies to a

clear glass, and the systems thus obtained are regarded as examples of compound disperse systems.

H. M. D.

**Theory of the Production and the Stability of Colloidal Solutions.** I. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1910, 1, 396—422).—A theoretical paper in which the author discusses the so-called dispersion and condensation methods for the production of colloidal solutions. Condensation methods are regarded as dependent on the retardation of crystallisation processes, and dispersion methods on the retardation of processes of solution.

H. M. D.

**Coexistence of the Crystalline and Colloidal States.** H. SCHADE (*Koll. Chem. Beihefte*, 1910, 1, 391—395).—Microscopic observations show that the formation of crystals of cholesterol from an alcoholic solution is preceded by a separation of the substance in the form of liquid drops. Similar effects are found in the case of solutions in ethyl ether and in oils, and also when the pure molten substance is rapidly cooled. The freshly-formed, needle-shaped crystals are very plastic, but this plasticity diminishes with time. The plastic condition is supposed to be associated with the presence of a portion of the cholesterol in the colloidal state, the colloidal form being gradually transformed into the crystalline modification.

H. M. D.

**Moulding of Gels by Crystals.** RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 96—98).—Observations are recorded which show that the crystallisation of substances from jellies, in consequence of the removal of water, frequently leads to the formation of characteristic gelatin aggregations.

H. M. D.

**Formation of Concretions in the Process of the Separation of Emulsion Colloids.** H. SCHADE (*Koll. Chem. Beihefte*, 1910, 1, 375—390).—The author discusses the part played by colloids in the formation of the special structures which are found in gall-stones, pearls, and hail-stones.

H. M. D.

**Influence of the Degree of Dispersion on the Stability of Chemical Compounds and the Decomposition of the Elements.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 93—96).—A theoretical paper in which the author examines the influence of the degree of dispersion of a dissolved or volatile substance on the equilibrium between the liquid or vapour containing the disperse substance and the corresponding solid phase. Conditions under which compounds and elements must dissociate as a consequence of the character of the disperse phase are indicated.

H. M. D.

**Alkali Hydroxides. I. The Binary Systems: Sodium and Potassium Hydroxides; Potassium and Rubidium Hydroxides, and Sodium and Rubidium Hydroxides.** GEORG VON HEVESY (*Zeitsch. physikal. Chem.*, 1910, 73, 667—684).—The complete equilibrium curves of the three binary systems in question have been determined. The substances were heated in a silver vessel in an



atmosphere of nitrogen, and the temperature measurements were made with a silver-nickel thermocouple, which is very suitable for working between  $-80^{\circ}$  and  $920^{\circ}$ . All four alkali hydroxides have a transition point at temperatures below the respective melting points, and the positions of these transition points in the binary systems have also been determined and are represented graphically.

The melting points and transition points of the pure substances are as follows: sodium hydroxide,  $318.4 \pm 0.2^{\circ}$ ,  $299.6 \pm 0.5^{\circ}$ ; potassium hydroxide,  $360.4 \pm 0.7^{\circ}$ ,  $248 \pm 0.5^{\circ}$ ; rubidium hydroxide,  $301 \pm 0.5^{\circ}$ ,  $245 \pm 0.5^{\circ}$ ; caesium hydroxide,  $272.3 \pm 0.3^{\circ}$ ,  $223 \pm 0.5^{\circ}$ . Rubidium hydroxide has  $D^{25}_D$  3.203; for caesium hydroxide,  $D^{25}_D$  3.675.

Sodium and potassium hydroxides are completely miscible both in the liquid and solid states; the freezing-point curve has a minimum at  $187^{\circ}$  and 38.7 atom per cent. of potassium hydroxide. The transition curve is of the same form as the freezing-point curve.

Potassium and rubidium hydroxides are also completely miscible both in the liquid and solid states, but the freezing-point curve shows two maxima at  $399^{\circ}$  and 87 atom per cent. and  $351^{\circ}$  and 22.3 atom per cent. of potassium hydroxide, as well as a minimum at  $306^{\circ}$  and 65.6 atom per cent. of potassium hydroxide. The transition diagram is of similar form. There is no definite evidence as to whether the maxima correspond with definite compounds of the two hydroxides.

Sodium hydroxide and rubidium hydroxide are not miscible between 80.8 and 37.6 atom per cent. of the latter compound. There is a maximum on the curve at  $278^{\circ}$  and 30.7 atom per cent. of rubidium hydroxide, which may correspond with the formation of a compound,  $(\text{NaOH})_2\text{RbOH}$ , although the evidence is not conclusive. There is no maximum on the transition diagram of this system.

From the thermal data, the latent heat of fusion and the heat of transition have been calculated by methods given by Tamman (compare Abstr., 1905, ii, 229; this vol., ii, 17). The latent heats of fusion per mol. are 1602, 1606, 1614, and 1609 cal., and the heats of transition per mol. are 990, 1522, 1702, and 1763 cal. for sodium, potassium, rubidium, and caesium hydroxides respectively. G. S.

**The Equilibrium of the Reciprocal Salt Pairs:**  $\text{KCl} + \text{NaNO}_3 \rightleftharpoons \text{KNO}_3 + \text{NaCl}$ . KENJIRO UYENA (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 245—261).—The following measurements have been made, the temperature being  $25^{\circ}$ : (1) The composition of the saturated solution when both sodium and potassium chloride are present as solid phases. One hundred grams of water contain 29.88 grams of sodium chloride and 16.28 grams of potassium chloride (compare Soch, Abstr., 1899, ii, 84). (2) The solubility in solutions of varying concentrations of potassium chloride in sodium chloride, and vice versa. (3) The composition of the saturated solution when both potassium chloride and nitrate are present as solid phases. One hundred grams of water contain 34.62 grams of potassium chloride and 23.88 grams of potassium nitrate (compare Soch, *loc. cit.*). (4) The solubility in solutions of varying concentrations of potassium nitrate in potassium chloride, and vice versa. (5) The composition of the saturated solution when both potassium and sodium nitrates are present as solid phases. One

hundred grams of water contain 100.10 grams of sodium nitrate and 46.35 grams of potassium nitrate. (6) The solubility in solutions of varying concentrations of sodium nitrate in potassium nitrate, and vice versa. (7) The composition of the saturated solution when both sodium nitrate and chloride are present as solid phases. One hundred grams of water contain 23.74 grams of sodium chloride and 56.56 grams of sodium nitrate (compare Soch, *loc. cit.*). (8) The solubility in solutions of varying concentrations of sodium chloride in sodium nitrate, and vice versa. (9) The composition of the saturated solution when sodium chloride, sodium nitrate, and potassium nitrate are together present as solid phases. One hundred grams of water contain 23.59 grams of sodium chloride, 63.26 grams of sodium nitrate, and 42.55 grams of potassium nitrate. (10) The solubilities in solutions of varying concentrations of sodium nitrate and potassium nitrate together in sodium chloride, of sodium chloride and sodium nitrate together in potassium nitrate, and of sodium chloride and potassium nitrate together in sodium nitrate. (11) The solubilities in solutions of varying concentrations of sodium chloride and potassium chloride together in potassium nitrate, and of potassium nitrate and potassium chloride together in sodium chloride.

The results are expressed graphically in various diagrams.

T. S. P.

**Equilibrium Solid-Liquid-Gas in Binary Systems which Present Mixed Crystals.** HUGO R. KRYTT (*Proc. K. Akad. Vetensk. Amsterdam*, 1910, 13, 206—210).—The equilibrium between *p*-dichloro- and *p*-dibromo-benzene when mixed crystals, liquid, and vapour are present has been investigated. Data are recorded which show the dependence of the initial melting point and the initial solidifying point on the composition of the mixed crystals, and, further, the pressure and composition of the vapour which is in equilibrium with mixed crystals of varying composition and the corresponding liquid phase.

In the estimation of the composition of the saturated vapour, a measured volume of this was passed through a heated tube containing calcium oxide; the calcium chloride and bromide thus obtained were determined by adding a known excess of silver nitrate to the nitric acid solution, weighing the precipitate obtained, and estimating the excess of silver by Volhard's method.

H. M. D.

**Equilibrium in the Ternary System: Water, Potassium Carbonate, Potassium Ethyl Dipropylmalonate.** J. W. M'DAVID (*Proc. Roy. Soc. Edin.*, 1910, 30, 440—447).—When a concentrated aqueous solution of potassium ethyl dipropylmalonate is shaken with a concentrated aqueous solution of potassium carbonate, two distinct layers are formed (compare Crichton, *Trans.*, 1906, 89, 929). The peculiarity of this case lies in the fact that both substances are salts of the same metal.

The composition of the two layers has been determined for different concentrations of the three components. The percentage of potassium ethyl dipropylmalonate was determined by precipitating a weighed quantity of the solution with dilute sulphuric acid, and titrating the

hydrogen ethyl dipropylmalonate with baryta. The potassium carbonate was determined by titration with acid, using phenolphthalein as indicator.

In order to produce equilibrium when a mixture is diluted, some potassium carbonate passes from the lower to the upper layer. In concentrated solutions there is a considerable quantity of potassium carbonate in the upper layer, whereas the amount of potassium ethyl dipropylmalonate in the potassium carbonate (lower) layer is very small, and it is only when the solutions are comparatively dilute that there is any appreciable increase in the amount of ester salt in the lower layer. At 25° the two layers become identical when the solution contains 11.6% of potassium ethyl dipropylmalonate, 20.6% of potassium carbonate, and 67.9% of water.

The effect of temperature on the equilibrium was determined, experiments being carried out at 2°, 25°, and 56°. When the mixture is such that the upper layer contains about 48% of potassium ethyl dipropylmalonate, the effect of temperature is very small. The critical solution at 25° becomes opalescent at 25.4°, but there is no apparent change on cooling to zero.

The temperature at which the two solid phases and the two liquid phases are present at the same time is probably in the vicinity of 46°; it could not be determined exactly, owing to the extreme viscosity of the liquid. Owing to the same cause, the solubility of the pure potassium ethyl salt could not be determined.

Solutions of sodium ethyl dipropylmalonate have the same properties with regard to a solution of sodium or potassium carbonate as the potassium ethyl salt has to either of these solutions. T. S. P.

Conditions for the Precipitation of Uric Acid and its Salts from Solutions. WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1910, 67, 332—403. Compare His and Paul, *Abstr.*, 1900, i, 591; Gudzent, *ibid.*, 1909, i, 434, 435; Little, *ibid.*, 1909, ii, 331).—The system water, phosphoric acid, sodium hydroxide, and uric acid has been examined; the concentration of the phosphoric acid was kept constant, so that the system could be regarded as one of three components, and the results represented graphically in a triangle. Phosphoric acid was never found in the solid phase.

A series of solubility determinations were made with the phosphoric acid of given concentration (2.076 grams of phosphoric oxide per litre) as solvent. All experiments show that uric acid readily tends to form supersaturated solutions, but after some time, or in the presence of air, the supersaturation disappears, and it may be due to the presence of metastable lactamurates (Gudzent).

Attempts made to determine the concentration of the solution in equilibrium with uric acid and monosodium urate in the presence of the given amount of phosphoric acid showed that the same solution is not obtained when uric acid is shaken with a solution of dihydrogen phosphate as is formed when uric acid is shaken with the disodium phosphate. The equilibrium solution was calculated, however, with the aid of Gudzent's and His and Paul's determinations. The value found was, for 100,000 molecules, 34.2 mols.  $\text{Na}_2\text{O}$ , 1.76 mols. uric

acid, and 26.3 mols.  $P_2O_5$ . The solubility curves of uric acid and of monosodium urate are given.

The results are given in the form of diagrams, and the meaning of these is discussed. It is pointed out that the solid phase which is deposited, its amount, and the concentration of uric acid in the final solution are all given by means of the diagram.

Similar experiments have been made with the potassium compounds. The equilibrium solution contains 38.67 mols.  $K_2O$ , 3.20 uric acid, and 26.3  $P_2O_5$ .

The results give some idea of the behaviour of uric acid in urine, but in this case the phenomena are more complex, owing to the presence of neutral salts, for example, sodium chloride, and of colloids.

The sedimentum lateritium, which consists mainly of quadrate, is metastable in the system sodium (potassium) oxide, phosphoric acid, uric acid, water. In urine it is rather more stable.

The quadrate is formed frequently when uric acid is precipitated, owing to rapid cooling.

Solubility determinations in the system sodium oxide, uric acid, and water have been made, and the solubility curve of monosodium urate determined. Even in the presence of strongly alkaline liquids the disodium urate is never met with as the solid phase.

J. J. S.

**Velocity of the Reaction between Colloidal Sulphur and Silver Sulphate.** M. RAFFO and A. PIERONI (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 158—160).—Colloidal sulphur, obtained by the action of sulphuric acid on sodium thiosulphate, reacts with a solution of silver sulphate according to the equation:  $3Ag_2SO_4 + 4H_2O + 4S = 4H_2SO_4 + 3Ag_2S$ . In dilute solution the precipitate first formed has a yellow colour, but this quickly changes to red, and finally to black. Measurements of the rate at which the silver sulphate is reduced show that the reaction proceeds according to the equation for a unimolecular change. From this it is evident that the reaction takes place in stages, and the differently coloured precipitates are supposed to represent the intermediate products.

Colloidal sulphur reacts with a solution of stannous chloride on warming, with the evolution of hydrogen sulphide and the precipitation of stannous sulphide. It liberates iodine from a solution of iodic acid, and yields hydrogen sulphide quite readily with nascent hydrogen. These experiments show that colloidal sulphur is much more reactive than other forms of sulphur.

H. M<sup>c</sup> D.

**Velocity of Saccharification of Starch.** I. HENRI VAN LAEB (*Bull. Acad. roy. Belg.*, 1910, 611—641).—Brown and Glendinning have shown (*Trans.*, 1902, 81, 388) that the hydrolysis of starch by diastase does not take place in accordance with the logarithmic law, whilst V. Henri (*Lois générales de l'action des diastases*, Paris, 1903) takes the view that it does, and suggests that the discrepancy in results may be due to differences in (1) method of determining the limiting value of the hydrolysis; (2) temperature, or (3) the ferment used. The present investigation has been undertaken to determine the origin of the discrepancy, and in this part the hydrolysis of starch by dilute

acids is dealt with, and it is shown that this follows the same law as the hydrolysis of sucrose by dilute acids, whatever may be the physical condition of the starch employed.

Special precautions were taken to guard against initial alkalinity of the starch used. It was observed that an opalescent starch solution (2%), prepared under a pressure of 4 atmospheres, showed no reducing power, passed easily through filter paper, was retained completely by parchment paper, gave a filtrate containing 0.375% of starch when filtered through collodion membrane, underwent no apparent change even under a pressure of 2 atmospheres at atmospheric temperature when mixed with hydrochloric acid, but became less opalescent and in time as limpid as water (although it still gave a blue colour with iodine) when mixed with diastase.

The results of the quantitative experiments made, which are tabulated in detail in the original, showed that (1)  $k$  varied very little with the time; (2) hydrolysis proceeded in the same manner whether starch maeilage, "soluble starch," or "soluble starch filtered through a collodion membrane" was the initial product used; (3) the rate of hydrolysis remained proportional to the concentration of starch when this did not exceed 5.6%, but fell off for higher concentrations; (4) the hydrolytic power of different acids for starch was proportional to their hydrolytic power for sucrose or their electric conductivity; (5) the rate of hydrolysis by sulphuric acid always increased with the concentration of the acid, but more slowly than this for dilute starch solutions, and more rapidly than this for concentrated starch solutions.

T. A. H.

**Specific Stereochemical Behaviour of Catalysts.** LEOPOLD ROSENTHALER (*Zeitsch. physikal. Chem.*, 1909, 73, 760—761).—Fajans (this vol., ii, 599) has suggested that the "asymmetric synthesis" of *d*-benzaldehydecyanohydrin discovered by the author is really due to an asymmetric decomposition of the symmetrical nitrile assumed as the primary product of the reaction, but it is now shown that this suggestion is untenable.

G. S.

**The Relative Principle and the Representation of Physical Phenomena in Space of Four Dimensions.** PHILIPP FRANK (*Zeitsch. physikal. Chem.*, 1910, 74, 466—495).—A theoretical paper in which a method of representing phenomena in space of four dimensions is described, and the advantages illustrated by application to optical phenomena in moving bodies and to certain electrodynamic phenomena.

G. S.

**Shape of the Molecule.** RICHARD D. KLEEMAN (*Phil. Mag.*, 1910, [vi], 20, 445—450).—If  $\sigma$  is the radius of the sphere of action of a molecule of a liquid, the molecular volume of which is  $V$ , then at corresponding temperatures the ratio  $V/\sigma^3$  should be the same for all liquids if the molecules are spherical in shape.

An examination of a number of different organic compounds from this point of view indicates that the molecules are not spherical. The relationships involved are, however, consistent with the assumption that the molecules consist of oblate spheroids.

H. M. D.

Gas Washing Bottles with Very Slight Resistance to the Passage of a Gas. ALEXANDER CHARLES CUMMING (*Trans. Faraday Soc.*, 1910, 6, 10-13).—Three modified forms of gas washing apparatus are described which are designed to produce the maximum washing effect with the minimum back pressure. In all of these the gas passes through a by-pass arranged near the surface of the washing liquid, and by its passage causes the liquid to circulate, so that the by-pass is continuously refilled from the main reservoir. R. J. C.

### Inorganic Chemistry.

The Constitution of Water (*Trans. Faraday Soc.*, 1910, 6, 71-123).—The following five papers formed the basis of a general discussion on the constitution of water.

Constitution of Water. Is Water an Electrolyte? PAUL WALØEN (*Trans. Faraday Soc.*, 1910, 6, 71-78).—According to the Thoms and Nernst rule, liquids with a dielectric constant as high as water ( $D=80$ ) should have great dissociating power on dissolved water, and enable it to function as an electrolyte. Water dissolved in liquid hydrogen cyanide ( $D=95$ ) has a very small or zero conductivity, whereas the conductivities of binary salts in the same solvent are very high. The conductivity of water dissolved in formamide ( $D>84$ ) is very small, and practically does not increase with dilution. In formic acid ( $D=58.5$ ) the conductivity of water is at least ten times as great, although the ionising power of the solvent is less. Nitrosodimethylamine ( $D=53.3$ ), although of less viscosity than formic acid, gives water solutions of less conducting power.

The conductivity of water dissolved in sulphuric acid ( $D>84$ ) is of a much higher order than any of the above, but the conductivities of all the substances mentioned dissolved in water are parallel to the conductivities when water is the solute.

The physical theory failing to account for the above facts, a chemical hypothesis is necessary. The author suggests that water becomes a good electrolyte when its solvent is distinctly acidic or basic. The amphoteric water must previously form with the solvent a kind of salt. The same chemical forces act when water is the ionising solvent. R. J. C.

The Chemical Nature of Molecular Association: a Special Study of the Case of Water. PHILLIP A. GUYE (*Trans. Faraday Soc.*, 1910, 6, 78-85).—Estimates of the degree of polymerisation of liquids based on the surface-tension values are subject to an unknown error, due to the difference in composition between the surface layer and the main bulk of the liquid.

Dutoit and Mojoi's formula connecting molecular weight with

surface tension gives a lower association factor than that of Ramsay and Shields, and leads to the conclusion that water at  $0^\circ$  is mainly trihydrol, and at the boiling point dihydrol. Since polymerisable substances are the more associated the greater the number of centres of association they contain, dihydrol should polymerise more readily than monohydrol. The formation of highly complex stable polyhydrole may accompany the phenomena of colloidal hydrates. The equilibrium of hydrol ( $\text{H}_2\text{O}$ ) and dihydrol ( $\text{H}_2\text{O}_2$ ) in the liquid phase is subject to the equation  $C_2 = KC_1^2$ , where  $C_1$  and  $C_2$  are the concentrations of hydrol and dihydrol respectively. In the gaseous phase  $C_2 = K^1(C_1)^2$ . Assuming that  $K^1$  has the same value as  $K$ , it may be calculated that the association factor of the liquid phase  $\alpha = [3v(1+y) - y^2 - y\sqrt{4v(1+y) + y^2}] \div \{v(1+y) - 2y^2\}$ , where  $y$  is the ratio of concentration of hydrol to dihydrol in the gaseous phase, and  $v$  the volume of vapour formed from unit volume of liquid at the same temperature. From the published values of  $y$  and  $v$ , the author calculates that the association factor of liquid water is 1.90 at  $80^\circ$ , 1.86 at  $100^\circ$ , and 1.82 at  $120^\circ$ , values very close to those obtained by Dutoit and Mojoiu.

According to the above equation, the polymerisation of only 1% of the vapour molecules corresponds with an association factor 1.58 in the liquid phase. As little as 1 in 10,000 polymerised gaseous molecules corresponds with an appreciable polymerisation of the liquid. Pressure has but little influence on the degree of association, but since the pressure in the surface film is greater than in the bulk of the liquid, the polymerisation in the surface layer will be higher, as indicated by the values calculated by Ramsay and Shields.

R. J. C.

**Liquid Water a Ternary Mixture: Solution Volumes in Aqueous Solutions.** WILLIAM R. BOUSFIELD and THOMAS M. LOWRY (*Trans. Faraday Soc.*, 1910, 6, 85—104. Compare Abstr., 1905, ii, 135).—It has been shown that the abnormal contraction in water between  $0^\circ$  and  $4^\circ$  is eliminated when 2% or more of dissolved sodium hydroxide is present, and also that the solution volumes of moderately concentrated sodium hydroxide attain a maximum value at about  $70^\circ$ .

Solution volumes represent the actual volume occupied by the solute minus the contraction which takes place during dissolution, and are more symptomatic of changes in the solvent (depolymerisation and association with solute) than in the solute. The simpler character of the solution-volume curves of concentrated solutions suggests that changes in hydration are of less importance than changes in the molecular weight of the solvent, and that the observed diminution in solution volumes at the higher temperatures takes place in spite of progressive dehydration which would lead to an increase in volume. The authors have already suggested that not only is dissolved ice present in liquid water at low temperatures, but dissolved steam molecules at temperatures approaching the boiling point. The same suggestion was made by Callendar (*Phil. Trans.*, 1902, A, 199, 147) in discussing the specific heat and thermal expansion of water, and the

compressibility values strengthen this view. The density of combined water is calculated to be 1.1 in the case of potassium chloride associated with about 10 molecular proportions of water. This is taken as the density of dihydrol, ice ( $\text{H}_2\text{O}_2$ ) and steam ( $\text{H}_2\text{O}$ ) occupying greater bulk.

Measurements have been made of solution volumes of chloral hydrate, sucrose, acetic acid, silver nitrate, and potassium, sodium, lithium, and calcium chlorides. The salts all show a maximum in the solution-volume curve, which is the more pronounced the lower the concentration, that is, the greater the relative disturbance of the condition of the solvent. The solutes, acetic acid, chloral hydrate, and sucrose, with small affinity for water exhibit no maxima, but the solution-volume curves have a distinct tendency to droop. Passing to the more hydrated solutes, the maximum occurs at lower and lower temperatures until with lithium chloride it is at  $35^\circ$ . This appears to be almost the limit possible, since any further lowering would be rendered difficult by the increasing proportions of ice molecules in the solvent.

R. J. C.

**Constitution of Water.** WILLIAM SUTHERLAND (*Trans. Faraday Soc.*, 1910, 6, 105—116. Compare *Abstr.*, 1906, ii, 603).—The author maintains his view that liquid water is a mixture of dihydrol and trihydrol. A geometrical structure representing a trihydrol molecule, the atomic diameter of oxygen and hydrogen being derived from the gas constants, gives 1.2 as the density as compared with 0.917, the actual density of ice. If the molecule were spinning in every plane it would sweep out a sphere, and its density would work out at a much lower figure than 0.917, so that a molecule of ice must be relatively fixed and its energy internal.

Since ionisation, when possible, is supposed to be complete, the proportion of hydrol in water (completely ionised) must be very small, the proportion of  $\text{H}^+$  and  $\text{OH}^-$  ions being known to be very small. Highly polymerised chains of hydrol molecules probably occur in colloidal hydrosols and hydrogels, each end of the chain being electrically attached to an amphoteric nucleus which the author terms a "semplar."

The density of water of crystallisation in thirty-one salts examined by Clarke is practically constant, 13 grams occupying 13.76 c.c. In  $\text{LiSO}_4 \cdot \text{H}_2\text{O}$  the volume of water (13.3 c.c.) is very near the mean. It is argued that water of crystallisation is always in the same form as in lithium sulphate, that is, solid hydrol of density 1.31. Liquid hydrol would have density about 1.26, that is, higher than dihydrol. Water of crystallisation has a dielectric capacity of the same order as sodium chloride, whereas that of liquid water is twelve times as great. The molecular refraction of water of crystallisation is about 4.22, whereas in liquid water, and ice the value is about 6.0. The specific heat of water of crystallisation, of ice and steam at constant pressure are each about 0.5, so that liquid water is abnormally high.

In melted crystals the water has specific heat about 1.0, indicating that a profound change occurs in water of crystallisation on melting.

R. J. C.



**The Specific Heat of Ice, Water, and Water Vapour.** WALTHER NERNST (*Trans. Faraday Soc.*, 1910, 6, 117—119. Compare this vol., ii, 263).—The molecular heat-temperature curves of ice, water, and steam are mapped from the most recent data. The water and ice curves are interpolated to absolute zero (molecular heat = 0).

In the case of steam, assuming that the molecules possess energy of rotation in three planes at right angles, the molecular heat cannot be less than  $8R/2 = 7.94$ , and this value is practically reached at room temperature. The molecular heat is, therefore, supposed to remain constant, and the curve is a straight line from  $350^\circ$  abs. to absolute zero.

The course of the molecular heat curves is in agreement with the hypothesis of a polymerisation:  $2H_2O = (H_2O)_2 + 2519$  cal. By means of the data given it is possible to calculate the vapour-pressure curves of ice and water down to very low temperatures. R. J. C.

**Ultra-microscopy of Iodine Solutions. II.** J. AMANN (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 67—70. Compare this vol., ii, 496).—

Further observations are recorded relating to the appearance of iodine solutions when examined by the ultra-microscope, and to the changes which are brought about by the action of light. The solvents used were chloral, molten chloral hydrate, phosphorus chloride, phosphoryl chloride, iodine trichloride, amyl acetate, pyridine, nitrobenzene, acetaldehyde, chloral alcoholate, propylamine, sulphuric acid, and peppermint oil. On the basis of the colour of the solutions and the ultra-microscopic observations, the solvents examined in this and the previous paper are divided into six groups, and those are then subdivided, so that in all seventeen different types of iodine solutions can be distinguished. H. M. D.

**Some Analogies between Derivatives of Oxygen and Nitrogen.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 29—36).—Attention is drawn to the analogy, displayed in many of their reactions, between hydrogen peroxide, hydroxylamine, and hydrazine. R. V. S.

**Exact Atomic Weights of Oxygen and Silver.** GUSTAV D. HINRICHS (*Compt. rend.*, 1910, 151, 513—515. Compare Abstr., 1907, ii, 945; Dubreuil, Abstr., 1909, ii, 653, 654).—In a previous paper (Abstr., 1909, ii, 653) the author has described a method for calculating the analytical excess ( $=\epsilon$ ), or difference between the experimental and absolute values of the atomic weights. A table is now given containing a résumé of the values of  $\epsilon$  calculated from 656 determinations of the atomic weights of oxygen and silver made between 1810—1910. The conclusion is drawn that the true atomic weights of these elements are 16 and 108 respectively, since in 70% of the determinations  $\epsilon$  is negligibly small. W. O. W.

**\*Solubility of Oxygen in Molten Silver.** FREDERICK G. DONNAN and T. W. A. SHAW (*J. Soc. Chem. Ind.*, 1910, 29, 987—990).—The

solubility of oxygen in fused silver was determined by measuring the contraction occurring when silver is fused in an atmosphere of oxygen. Ten grams of melted silver at 1020° and under a pressure of 751 mm. absorb 20.5 c.c. of oxygen (measured at 0° and 760 mm.), a result which is practically identical with that obtained by Sieverts and Hagsnacker (Abstr., 1909, ii, 1004). From the results of Sieverts and Hagsnacker it is calculated that the freezing point of silver saturated with air (only the oxygen is absorbed) should be lowered by 10.4°; the experimental number is 7°.

T. S. P.

**Complexity of Tellurium.** WILLIAM R. FLINT (*Amer. J. Sci.*, 1910, [iv], 30, 209—219. Compare Browning and Flint, Abstr., 1909, ii, 996).—Five hundred grams of purified tellurium were oxidised by nitric acid and converted into the tetrachloride by repeated evaporation with hydrochloric acid. The solution was diluted with a large volume of boiling water, and the precipitated dioxide dissolved in slight excess of hydrochloric acid and reprecipitated by further addition of a large volume of water. After a series of ten fractionations by this hydrolytic method, 23 grams of dioxide were obtained. By the basic nitrate method, the atomic weight of the metal in this sample of dioxide was found to be 124.32, whereas the same method, applied to the original material, gave 127.45. The author considers that the complexity of tellurium, purified by the usual methods, has been definitely established by these results, and the value 124.3 represents the nearest approach which has yet been made to the true atomic weight of tellurium. In support of the view that fractional hydrolysis of the chloride leads to a gradual separation, it is found that the product obtained after four fractionations gave an atomic weight 126.59, and after eight fractionations 125.37.

Preliminary experiments relating to the less readily hydrolysed fraction are also described. The tellurium in the filtrates from the above hydrolytic processes was recovered by treatment with ammonia and acid, the dioxide dissolved in hydrochloric acid, and the solution diluted with a large volume of boiling water. The filtrate from the precipitated dioxide was then heated to boiling, ammonia and acetic acid added, and the less easily hydrolysed fraction thus obtained was subjected to three further operations of the same kind. By this series of fractionations a sample of dioxide weighing about 10 grams was obtained. On fractionating this by addition of successive quantities of ammonia to the boiling hydrochloric acid solution, 8 grams of an orange-coloured, crystalline substance, 2 grams of a yellow, crystalline substance, and 0.1 gram of a pale green, substance were obtained. These substances were tested for iron, copper, bismuth, and antimony with negative results. In hydrochloric acid solution all three give black precipitates with stannous chloride similar to that obtained with ordinary tellurium. On addition of excess of ammonia to the solution of the green substance, the precipitate obtained is not completely dissolved by the excess of alkali. Both the soluble and insoluble portions, when dissolved in hydrochloric acid, give a black precipitate with stannous chloride. These results indicate that tungsten is not present.

H. M. D.

**Relations between White Phosphorus, Red Phosphorus, and Pyromorphic Phosphorus.** PIERRE JOLIBOIS (*Compt. rend.*, 1910, 151, 382—384. Compare Cohen and Olie, *Abstr.*, 1909, ii, 998).—The author denies the validity of Cohen and Olie's conclusion that red phosphorus is not an individual modification. This view is not in agreement with the observations already published (*Abstr.*, 1909, ii, 726) or with new experiments described in the present communication.

The vapour pressure at different temperatures has been determined for red and white phosphorus, and for the new pyromorphic form (*loc. cit.*). The results are plotted in logarithmic curves, from which the conclusion is drawn that the latter is stable below  $450^{\circ}$ , the ordinary red modification between  $450$ — $610^{\circ}$ , whilst white phosphorus is in equilibrium above  $610^{\circ}$  (compare Chapman, *Trans.*, 1899, 75, 734). The same results were obtained in direct determinations of the transition points. Hittorf's phosphorus, obtained by crystallisation from lead, appears to be a mixture of ordinary crystallised phosphorus with the pyromorphic variety. The abnormally high density is due to the presence of lead. W. O. W.

**The Hydrates of Disodium Hydrogen Phosphate.** ICHITARO KITAWAKI (*Mem. Coll. Sci. Eng. Kyoto*, 1909—1910, 2, 237—239).—Shiomi (*Abstr.*, 1909, ii, 573) has observed three breaks in the solubility curve of disodium hydrogen phosphate, namely, at  $36.45^{\circ}$ ,  $48.0^{\circ}$ , and  $95.2^{\circ}$ . The break at  $36.45^{\circ}$  corresponds with the transition from dodecahydrate to heptahydrate, and it is now found that the two other breaks correspond with the transitions from heptahydrate to dihydrate, and from dihydrate to anhydrous salt respectively.

The dihydrate was isolated by fusing the dodecahydrate in its water of crystallisation and evaporating the resulting solution at a temperature of  $70$ — $75^{\circ}$ . The anhydrous salt was obtained from a similar experiment carried out in the neighbourhood of  $99.5^{\circ}$ . T. S. P.

**The Boiling Point of Sodium Chloride.** FRIEDRICH EMICH (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1910, ii, 65).—Using Burgess' method (*Abstr.*, 1908, ii, 41), the boiling point of sodium chloride was found to be  $1750^{\circ}$ . T. S. P.

**Action of Sodium Carbonate on Insoluble Carbonates.** WILLIAM OCHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 512—515).—The experiments were made on the same lines as with solutions of the alkali nitrates (see following abstract), boiling aqueous solutions of sodium carbonate being used. Barium and strontium carbonates are not attacked. Cadmium carbonate is only affected by strong solutions of sodium carbonate, some cadmium oxide being formed. Dolomite and magnesium, lead, and zinc carbonates are all attacked. With calcium carbonate (washed chalk) concordant results could not be obtained.

Calcium phosphate is attacked by boiling solutions of either sodium or potassium carbonate. T. A. H.

**Action of Lithium Nitrate on Insoluble Carbonates.**

WILLIAM OCHSENER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 332—334).

—In previous papers the results of investigations on the action of sodium or potassium nitrate on carbonates insoluble in water have been given (this vol., ii, 411, 612). On applying the same methods with boiling aqueous solutions of lithium nitrate, it was found that barium, calcium, magnesium, zinc, and lead carbonates were all attacked, whilst strontium and cadmium carbonates were not affected. It was necessary to use dilute solutions in the case of barium and very dilute solutions in the case of magnesium in order to detect these metals in presence of lithium.

T. A. H.

**Bolognian Stones. II. LUDWIG VANINO and EMILIE ZUMBUSCH (*J.***

*pr. Chem.*, 1910, [ii], 82, 193—204. Compare *Abstr.*, 1909, ii, 731).—

It has been shown previously that the quantity of sulphur employed in the preparation of Bolognian stones affects their luminescence. The quality of the sulphur is, however, immaterial, since at a high temperature all varieties of sulphur are changed into the same modification. The quality of the lime is of prime importance. Ordinary builder's lime and Kahlbaum's "calcium oxide *pro analysi*" are useless; ignited limestone forms good stones, but the best results are obtained with Kahlbaum's lime prepared from marble. The three last-mentioned limes are shown to be alike chemically, to exhibit the same flame spectrum, and in solution to have practically the same alkalinity and electrical conductivity. The difference in their efficiency must be attributed, therefore, to their difference in physical structure, on account of which the limes have different velocities of reaction. This explanation can be tested experimentally, since it is well known that calcium oxide prepared from the nitrate is remarkably inactive towards chemical reagents, whilst the oxide prepared from the carbonate or the hydroxide is easily attacked, and also since it has been shown (*loc. cit.*) that the phosphorescence of Bolognian stones is mainly due to the presence of polysulphides; thus it is found that stones manufactured from calcium oxide prepared from the nitrate are of poor quality, and contain very little polysulphide, whilst similar stones made from the oxide prepared from the hydroxide or carbonate phosphoresce extensively, and exhibit a strong polysulphide reaction. So also stones prepared from Kahlbaum's oxide, from marble, or from ignited limestone give immediately a white turbidity when treated with sodium carbonate and then acidified, whilst the inefficient stones prepared from oxide "*pro analysi*" give only a feeble polysulphide reaction many seconds after acidification.

The oxides of barium and of strontium, which are too fusible to be used alone in the preparation of Bolognian stones, have a very beneficial effect when employed in conjunction with the carbonates. Good stones are obtained from a mixture of strontium carbonate (20 grams), sulphur (3 grams), lithium carbonate (0.5 gram), and thorium nitrate (1 c.c. of 0.5% alcoholic solution), or from a mixture of barium carbonate (20 grams), sulphur (3 grams), lithium carbonate (0.5 gram), and rubidium carbonate (0.3 gram), but the phosphorescence of stones produced when one-half of the strontium or of the barium carbonate is

replaced by the corresponding hydroxide is still more intense, and exhibits a very much slower rate of decay.

Attention has also been given to the effects produced by the addition of minerals, containing rare earths or radioactive substances, to the mixtures used in the preparation of Bolognian stones. The addition of pitchblende, cleveite, or monazite almost or entirely destroys the phosphorescence; from mixtures containing fergusonite, moderately good stones can be prepared, but their quality is very much inferior to that of stones prepared from mixtures containing the usual salts of bismuth, thallium, etc.

Stones exceeding any others previously made in the intensity and duration of their phosphorescence have been prepared by the ignition, for three-quarters of an hour in a Rössler furnace, of the following mixture: calcium oxide (10 grams), strontium carbonate (10 grams), barium carbonate (10 grams), magnesium oxide (10 grams), sulphur (6 grams), potassium sulphate (1 gram), sodium sulphate (1 gram), lithium carbonate (2 grams), starch (2 grams), bismuth nitrate (2 c.c. of 0.5% solution), and thallium sulphate (2 c.c. of 0.5% solution). The stones exhibit a pale blue phosphorescence, which decays very much more slowly than that of even the best violet stones. When the ignition is prolonged to two hours, the phosphorescence is very intense and greenish-yellow; after three hours' ignition, the stones are no longer luminous. The finest and most intense green phosphorescence hitherto obtained is exhibited by stones prepared by igniting the following mixture for three-quarters of an hour: calcium hydroxide (10 grams), strontium oxide (10 grams), sulphur (3 grams), potassium sulphate (0.5 gram), sodium sulphate (0.5 gram), lithium carbonate (1 gram), starch (1 gram), bismuth nitrate (1 c.c.), rubidium nitrate (1 c.c.). The persistence of the phosphorescence is such that it is possible to read in darkness by the light of these stones one hour after their preparation.

Unsuccessful attempts have been made to intensify the phosphorescence of Bolognian stones by rubbing them with fluorescent substances, by keeping them in fluorescent solutions or in an atmosphere of hydrogen, carbon dioxide, or oxygen, and by gently warming them with potassium chlorate, potassium perchlorate, or barium peroxide.

The prejudicial effect of heat on Bolognian stones is shown by heating them in a fusible alloy of tin and lead, in molten zinc, and in molten silver; the phosphorescence, which is violet at lower temperatures, becomes blue and then pale blue at higher temperatures, and finally is changed to green shortly before its disappearance. Calcium stones can be kept at 80–100° for eight to ten hours without injury.

The sulphides of all the metals of the alkaline earths exhibit phosphorescence; stones prepared from magnesium oxide or sulphide, however, do not phosphoresce unless some calcium compound is present. C. S.

**Hydration and Constitution of Portland Cement.** SENDER KEISERMAN (*Koll. Chem. Beihefte*, 1910, 1, 423–453).—A summary is given of the more important views which have been put forward in

reference to the constitution and the hydration of Portland cement, and a new method of investigating the nature of the constituents of the material is described. This is based on the specific absorptive capacity which particular constituents possess for certain colouring matters. As the result of the examination of a large number of colouring substances, the author recommends patent-blue for the detection of alumina, alcoholic anthrapurpurin for free lime, neutral methylene-blue for free amorphous silica, and an acetic acid solution of methylene-blue for combined silica. From observations made with these reagents on the hydrated cement, the following conclusions are drawn. The fine needle-shaped crystals consist of hydrated calcium monosilicate; these are coloured by anthrapurpurin, but not by patent-blue. The amorphous constituent of the cement consists also of calcium monosilicate containing a larger proportion of water. The large, hexagonal crystals are calcium hydroxide, and the small, hexagonal plates are hydrated tricalcium aluminate. Experiments with the unhardened material (klinker) indicate that this in all probability consists of a conglomerate of dicalcium silicate and tricalcium aluminate in the ratio:  $4(2\text{CaO}, \text{SiO}_2) + 3\text{CaO}, \text{Al}_2\text{O}_3$ .

H. M. D.

The Solubility of Alkali Sulphates in Alkaline Solutions, and of Calcium Sulphate in Solutions of Alkali Sulphate and Free alkali. JON. D'ANS and O. SCHREINER (*Zeitsch. anorg. Chem.*, 1910, 67, 437—441. Compare this vol., ii, 125).—The isotherms at 25° have been determined for certain solutions of alkali sulphates containing an excess of alkali hydroxide. The solubility of sodium, potassium, and ammonium sulphates is progressively lowered by the addition of increasing quantities of the corresponding alkali. Basic salts are not formed.

Gypsum is the stable solid in contact with a saturated solution of sodium sulphate at 25°, but when sodium hydroxide is added, calcium hydroxide becomes the stable solid, the limit being at 1.41 mols.  $\text{Na}_2\text{SO}_4$  and 1.48 mols.  $\text{NaOH}$  in 1000 grams of solution. In solutions of potassium sulphate, the corresponding limit is between syngenite and calcium hydroxide. The change in concentration produced by adding ammonia to the limiting solution ammonium syngenite-gypsum is also determined.

C. H. D.

The Reaction between Strontium Sulphate and Sodium Carbonate. WALTER KENZ (*Zeitsch. anorg. Chem.*, 1910, 68, 69—72).—The ratio  $[\text{Na}_2\text{CO}_3]/[\text{Na}_2\text{SO}_4]$  in contact with strontium sulphate is found to be 0.0676 at 25°. The dissociation of the two salts may be neglected, being the same for both. From the above ratio,  $[\text{SrCO}_3]/[\text{SrSO}_4]$  is 0.26. Calculation from the known solubilities of strontium sulphate and carbonate gives 0.13, a result of the same order. Freshly precipitated and washed strontium sulphate gives the same result as when dried at 70° or heated to redness.

C. H. D.

Barium Nitride, and its Relation to Nitrogen in Presence of Iron. DAFFY WOLK (*Bull. So. chim.*, 1910, [iv], 7, 830—832. Compare Maquenne, Abstr., 1892, 776, and Guntz and Mentrel, Abstr., 1903, ii, 546).—It is shown that barium nitride may be

prepared by the direct action of nitrogen on heated barium amalgam. The amalgam used was prepared by Guntz' process (Abstr., 1902, ii, 138). It was heated in an iron crucible, surrounded by a nickel shell, the whole being placed in a porcelain tube, which was then thoroughly dried by passing in pure dry nitrogen and evacuating the tube. The temperature of the tube was gradually raised to  $800^{\circ}$  in the course of three hours and then to  $1000^{\circ}$ , when the nitrogen was rapidly absorbed, forming barium nitride,  $\text{Ba}_3\text{N}_2$ , as a brown powder, which was unstable in moist air, furnishing barium hydroxide and ammonia. The product contained a trace of ferric nitride, and the proportion of the latter was materially increased by (1) more rapid heating; (2) heating the barium amalgam in contact with a fragment of sheet iron. In such a mixed product the ferric nitride dissociated towards the end of the reaction, unless the quantity of barium nitride present was relatively high.

T. A. H.

**Colloidal Barium Sulphate.** YOGORO KATO (*Mem. Coll. Sci. Eng. Kyōto*, 1909—1910, 2, 187—215).—Colloidal barium sulphate (compare Feilmann, Abstr., 1909, ii, 482) was obtained by adding an alcoholic solution of sulphuric acid (obtained by diluting a molar aqueous solution with twice its volume of alcohol) to the equivalent quantity of a molar solution of barium acetate diluted with six times its volume of alcohol. The resulting precipitate and milky solution were evaporated to dryness under diminished pressure, keeping the temperature below  $40^{\circ}$ , giving a translucent, casein-like residue, which was readily and completely soluble in water to a fluorescent colloidal solution.

Barium sulphate is a positive colloid, and the solution shows the usual precipitation reactions towards anions. Cations of higher valency hinder the coagulation. Barium chloride and nitrate do not cause coagulation except in highly concentrated solutions; moreover, the presence of barium ions hinders the coagulation by potassium chloride. Highly dissociated electrolytes have generally the stronger coagulating effect, but sodium citrate has a much lower coagulating power than citric acid. Barium chloride and ferric sulphate, which are known to be much occluded by precipitated barium sulphate, have comparatively small coagulative power. Electrolytes which, owing to hydrolysis, contain colloids in solution have an abnormal coagulating power, which is strong when the colloid is negative and weak when it is positive.

The adsorption by the barium sulphate gel in solutions of potassium nitrate, potassium sulphate, and barium chloride was determined by measuring the specific conductivity of their solutions in which the gel was suspended. The adsorption was very small, but was found to be in fair agreement with the ordinary adsorption formula. Measurements of the electrical conductivity before and after coagulation showed that slight adsorption took place when the barium sulphate was coagulated by potassium sulphate.

T. S. P.

**Double Chlorides and Iodides of Zinc.** FRITZ FENHAIM and SAMUEL MODER (*Zeitsch. anorg. Chem.*, 1910, 67, 379—386. Compare Abstr., 1908, ii, 693).—Two calcium zinc chlorides,  $\text{CaZnCl}_6 \cdot 5\text{H}_2\text{O}$ .

and  $\text{Ca}_2\text{ZnCl}_6 \cdot 6\text{H}_2\text{O}$ , may be obtained by mixing the components in suitable proportions, and form very hygroscopic crystals. The corresponding *strontium*,  $\text{SrZnCl}_4 \cdot 4\text{H}_2\text{O}$ , and *barium* salts,  $\text{BaZnCl}_4 \cdot 4\text{H}_2\text{O}$ , are described, the latter being only obtained when a warm solution is evaporated.

In addition to Rammelsberg's salt,  $\text{KZnI}_3$ , a second *potassium zinc iodide*,  $\text{K}_2\text{ZnI}_4 \cdot 3\text{H}_2\text{O}$ , may be obtained by evaporating the solution on the water-bath until crystallisation begins, and then allowing it to remain for several days over sulphuric acid. It forms rather hygroscopic, transparent crystals, melting above  $100^\circ$ . Two *sodium zinc iodides*,  $\text{Na}_2\text{ZnI}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{NaZnI}_3 \cdot 2\text{H}_2\text{O}$ , of which the first was described by Rammelsberg, may be obtained. A second *ammonium zinc iodide*,  $\text{NH}_4\text{ZnI}_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , forms very hygroscopic hexagonal tablets. The *calcium*, *strontium*, and *barium* salts,  $\text{CaZnI}_4 \cdot 8\text{H}_2\text{O}$ ,  $\text{SrZnI}_4 \cdot 9\text{H}_2\text{O}$ , and  $\text{BaZnI}_4 \cdot 4\text{H}_2\text{O}$ , are described. C. H. D.

**Behaviour of Solid and Fused Copper towards Gases.** ADOLF SIEVERTS and WILHELM KRUMBHAAZ (*Zeitsch. physikal. Chem.*, 1910, 74, 277—307. Compare Stahl, *Metallurgie*, 1907, 4, 769).—At high temperatures ( $1200^\circ$ ) oxygen is taken up by fused copper with the formation of cuprous and cupric oxides, and is not given up when solidification takes place in an atmosphere free from oxygen because of the small dissociation pressure of the oxides. Nitrogen, carbon monoxide, and carbon dioxide are insoluble both in solid and fused copper.

Both solid and fused copper absorb hydrogen. At constant pressure the solubility of hydrogen in solid copper increases in a linear manner as the temperature rises; at the melting point there is a sudden increase in solubility, and beyond that point the solubility again increases linearly with the temperature as far as the measurements were carried ( $1500^\circ$ ). At  $623^\circ$ ,  $919^\circ$ , and the melting point, 100 grams of solid copper absorbs 0.084, 0.287, and 0.41 milligram of hydrogen, and at  $1123^\circ$ ,  $1276^\circ$ , and  $1520^\circ$ , 0.608, 0.862, and 1.350 milligrams of hydrogen respectively are absorbed by 100 grams of fused copper: in each case at 760 mm. pressure. At constant temperature the amount of hydrogen absorbed by fused copper is proportional to the square root of the pressure. As even at  $650^\circ$  hydrogen diffuses slowly out of a copper tube, it is assumed that copper and hydrogen form solid solutions.

Sulphur dioxide is insoluble in solid copper, but dissolves readily in fused copper, and in this case, also, the solubility increases as the temperature rises. At  $1123^\circ$ ,  $1276^\circ$ ,  $1327^\circ$ , and  $1500^\circ$ , 100 grams of copper dissolve 0.453, 0.627, 0.705, and 0.950 gram respectively of sulphur dioxide at 760 mm. pressure. It is remarkable that in this case also the solubility is proportional to the square-root of the pressure. In the case of hydrogen, it is usually assumed that the gas is present in the copper in the atomic condition, but a similar explanation is excluded for sulphur dioxide. G. S.

**Conditions which Determine the Composition of Electrodeposited Alloys. II. Silver-Copper.** SAMUEL FIELD (*Trans. Faraday Soc.*, 1910, 6, 1—9. Compare this vol., ii, 38).—Copper and silver are electrodeposited together only within very



narrow ranges of concentration, temperature, etc. With sulphates and nitrates, solutions containing an enormous preponderance of copper yield practically pure silver. With cyanides, copper begins to be deposited when the amount of silver is reduced to about 0.4 gram per litre. By further reduction of the silver concentration, deposits containing any proportion of copper are obtainable. The deposition of copper along with silver is promoted, not only by large excess of copper, but by decrease in the proportion of free potassium cyanide, increased current density, and low temperature of deposition. The conditions favourable to the deposition of copper in presence of silver are analogous to those necessary for the deposition of zinc in presence of copper. The silver compound used in the above experiments was prepared by dissolving washed precipitated silver cyanide in a minimum of potassium cyanide. The copper compound had the composition  $\text{CuCN} \cdot \text{KCN}$ . The deposits were always of a powdery character, usually on account of the high current density used.

R. J. C.

**Ternary Alloys of Copper, Antimony, and Bismuth.** NICOLA PARRAVANO and E. VIVIANI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 69—75. Compare this vol., ii, 779).—Owing to the existence of the compound  $\text{Cu}_3\text{Sb}$ , which melts without decomposition, the ternary system  $\text{Cu-Bi-Sb}$  is divided into two others, namely,  $\text{Cu-Cu}_3\text{Sb-Bi}$  and  $\text{Cu}_3\text{Sb-Sb-Bi}$ . From their experimental results given in the present paper, the authors have constructed the diagram of the binary system  $\text{Cu}_3\text{Sb-Bi}$ , which is necessary for the study of the ternary systems mentioned above. The compound  $\text{Cu}_3\text{Sb}$  and bismuth are only partly miscible in the liquid state, and they form neither compounds nor solid solutions. At  $640^\circ$  two layers are formed, one rich in  $\text{Cu}_3\text{Sb}$  (87%), and the other rich in bismuth (92%). The eutectic is nearly pure bismuth. In all the alloys there is an indication at  $390\text{--}400^\circ$  of the transformation of  $\beta\text{-Cu}_3\text{Sb}$  into  $\alpha\text{-Cu}_3\text{Sb}$ . Alloys which solidify below  $400^\circ$  deposit only  $\alpha\text{-Cu}_3\text{Sb}$ . In conclusion, the general form of the diagram of the ternary system  $\text{Cu}_3\text{Sb-Sb-Bi}$  is discussed.

R. V. S.

**Preparation of a Cuprous Nitrate,  $\text{CuNO}_2 \cdot 2\text{NH}_3$ .** W. H. SLOAN (*J. Amer. Chem. Soc.*, 1910, 32, 972—973).—The salt,  $\text{CuNO}_2 \cdot 2\text{NH}_3$ ,

has been prepared by leaving a solution of cupric nitrate in liquid ammonia in contact with copper foil until it became colourless. On allowing the ammonia to distil gradually from the solution, the cuprous nitrate crystallised. It was not obtained quite pure, but contained a few blue crystals of cupric nitrate. The salt rapidly undergoes oxidation in the air.

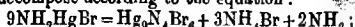
E. G.

**The Ammonia Compounds of Mercuric Bromide.** RAGNAR WIDMAN (*Zeitsch. anorg. Chem.*, 1910, 68, 1—25. Compare Gauduchon, *Abstr.*, 1909, ii, 670; this vol., ii, 296).—The following compounds

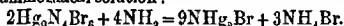
can exist in contact with solutions containing mercuric bromide, ammonium bromide, and ammonia in different concentrations:

$\text{HgBr}_2 \cdot 2\text{NH}_3$ ;  $\text{NH}_2\text{HgBr}$ ;  $\text{NH}(\text{HgBr})_2$ ;  $\text{Hg}_2\text{N}_4\text{Br}_6$ ; and  $\text{NHg}_2\text{Br}$ , and probably no others.

The compound  $\text{HgBr}_2 \cdot 2\text{NH}_3$  is formed on adding an excess of ammonia to a solution of mercuric bromide and much ammonium bromide. The compound  $\text{NH}_2\text{HgBr}$  is obtained from it by loss of ammonium bromide, in contact with a solution containing little of this salt. When the bromide concentration falls still lower,  $\text{NHg}_2\text{Br}$  is obtained. This compound is partly decomposed by water, yielding mercuric oxide. Concentrated ammonium bromide liberates ammonia from  $\text{HgBr}_2 \cdot 2\text{NH}_3$ , whilst water converts it into  $\text{NH}_2\text{HgBr}$ , which may further decompose according to the equation:



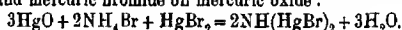
or, if sufficient ammonia is present:  $2\text{NH}_2\text{HgBr} = \text{NHg}_2\text{Br} + \text{NH}_4\text{Br}$ . Similarly, in ammoniacal solution:



It is not found possible to obtain  $\text{Hg}_2\text{N}_4\text{Br}_6$  by the action of mercuric bromide on  $\text{NHg}_2\text{Br}$ . Mercuric oxide and ammonium bromide react according to the equation:



In the presence of an excess of mercuric bromide, the following reaction takes place:  $3\text{NH}_2\text{HgBr} + \text{HgBr}_2 = 2\text{NH}(\text{HgBr})_2 + \text{NH}_4\text{Br}$ . This product is new. It is white, but differs from the other compounds in being sensitive to light. It is not converted into  $\text{Hg}_2\text{N}_4\text{Br}_6$  by the action of water. It is formed by the action of ammonium bromide and mercuric bromide on mercuric oxide:



C. H. D.

Colour Suddenly Assumed by Colourless Solutions of Coloured Substances at the Moment of Solidification of the Colourless Solvent. DÉSIRÉ GERNEZ (*Compt. rend.*, 1910, 151, 272—276; *Ann. Chim. Phys.*, 1910, [viii], 21, 283—288. Compare Abstr., 1903, ii, 428, 481).—The red modification of mercuric iodide behaves like metallic mercury with molten phosphorus (this vol., ii, 707), forming a solution which remains colourless if kept in a superfused condition. If solidification is induced, however, the yellow form is deposited. Solutions of mercuric iodide in formanilide, salol, menthol, thymol, or benzophenone behave in the same way. Solutions in liquid naphthalene, spermaceti, or the higher fatty acids are colourless, but become yellow if rapidly cooled. Such solutions, however, slowly become red if kept below the transition temperature of 126°.

W. O. W.

Scandium. II. RICHARD J. MEYER and HERBERT WINTER (*Zeitsch. anorg. Chem.*, 1910, 67, 398—417. Compare Meyer, Abstr., 1909, ii, 45; Crookes, *ibid.*, 44; this vol., ii, 714).—The mixture of rare earths obtained from the Zinnwald wolframite contains 56.4% of scandium oxide, whilst direct precipitation with sodium silicofluoride yields a product containing 93.3% of scandium oxide, equivalent to

0.1% of the whole mineral I and II. A similar proportion is found in the wolframite from Sadisdorf, near Schmiedeberg (analysis III).

	WO <sub>3</sub>	FeO	MnO	TiO <sub>2</sub> + Ta <sub>2</sub> O <sub>5</sub>	PbO + SnO	CaO	Rare earths.
I. 75.41	9.34	14.90	0.50	0.18	0.55	0.15	0.15
II. —	9.38	14.15	0.47	0.35	0.70	0.15	0.15
II. 78.47	15.13	9.81	0.63	0.47	0.54	0.20	0.20

Analysis IV represents an ancient tin slag from Zinnwald, containing 0.09% of scandium oxide. The part not estimated is mainly calcium phosphate.

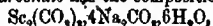
Metallo	SnO <sub>2</sub>	SiO <sub>2</sub>	WO <sub>3</sub>	FeO	MnO
IV. 8.6	8.6	16.0	30.0	13.4	9.0

Specimens of wilkite examined are free from scandium.

For the separation of thorium from scandium, extraction of the ignited oxides with hydrochloric acid results in complete solution, although thorium oxide is ordinarily insoluble. Hydrogen peroxide also fails to remove thorium, whilst the separation by extracting the oxalates with hydrochloric acid is incomplete. Most of the thorium may be removed by precipitation with iodic acid, and fractional sublimation of the anhydrous chloride also gives good results, scandium chloride being the less volatile.

[With M. SPETER.]—The best separation is obtained by boiling the carbonates with a solution of sodium carbonate, when a sparingly soluble scandium salt separates at a concentration at which thorium remains completely dissolved. The purity of the scandium oxide is tested spectroscopically and by its freedom from radioactivity.

Scandium sodium carbonate has the composition



and the ammonium salt,  $2\text{Sc}_2(\text{CO}_3)_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$ . A potassium salt is not obtainable under similar conditions. Two precipitations of the double carbonate yield a product of atomic weight 45, which is not changed by further precipitation. Crystallisation of the acetylacetonate from alcohol yields a product of the same atomic weight, thorium remaining in solution. The atomic weight is still 44.9 after six crystallisations, a result higher than that adopted on the basis of Nilson's older determinations. C. H. D.

**Preparation and Fusion of Aluminium Nitride.** DUFFY WOLK (*Compt. rend.*, 1910, 151, 318—319. Compare Kohn-Abrès, this vol., ii, 506, 715; Serpek, this vol., ii, 615).—In connexion with the question of priority, the author draws attention to his own communications. Aluminium begins to unite with nitrogen at 820—850°; absorption is rapid at 1000°, but at 1100° decomposition occurs. Ammonia has no specific action on aluminium. W. O. W.

**Double Bromides of Manganese.** FRITZ EPHRAIM and SAMUEL MODL (*Zeitsch. anorg. Chem.*, 1910, 67, 376—378).—Manganous bromide has little tendency to form double bromides. Negative results are obtained with potassium, barium, and strontium bromides.

Sodium and ammonium bromides appear to form mixed crystals with manganous bromide.

Calcium manganous bromide,  $\text{CaMnBr}_2 \cdot 4\text{H}_2\text{O}$ , forms pink crystals, and readily breaks up into its components. C. H. D.

**Complex Compounds of Manganese Salts with Hydroxy-acids.** OLOF TAMM (*Zeitsch. physikal. Chem.*, 1910, 74, 496—502).—As Euler and Bolin (*Abstr.*, 1909, i, 863) have shown that the laccase from *Medicago sativa* consists largely of salts of organic hydroxy-acids, the author has investigated the complexes formed with manganese salts by determining the constant of the equation  $[\text{Mn}(\text{OH})_2][\text{hydroxy-acid ion}]/[\text{complex ion}] = k$  for different hydroxy-acids at room temperature. The method employed was to shake freshly-precipitated and washed manganous hydroxide with equivalent normal solutions of the sodium salts of the respective acids until equilibrium was reached, and to determine the amount of manganese dissolved. The solubility of the hydroxide in water was also determined; it amounts to  $2 \cdot 10^{-4}$  mol. per litre. From the results, the following values of  $k$  were obtained: citric acid,  $2 \cdot 4 \times 10^{-3}$ ; tartaric acid,  $7 \cdot 1 \times 10^{-3}$ , and malic acid,  $11 \cdot 6 \times 10^{-3}$ .

It was found, however, that when manganous hydroxide is formed in the presence of the sodium salt of the hydroxy-acid a much greater amount remains dissolved. In the case of sodium citrate, about nine times as much hydroxide remained in solution as when the citrate was shaken with precipitated and washed manganous hydroxide.

G. S.

**The Spontaneous Decomposition of Permanganates and Permanganic Acid.** ANTON SKRABAL (*Zeitsch. anorg. Chem.*, 1910, 68, 48—51).—The author considers that the evolution of oxygen in the decomposition of permanganates is chiefly due to the reaction  $\text{Mn}^{\text{IV}} + \text{Mn}^{\text{VII}} \rightarrow \text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{II}} + \text{O}_2$  (*Abstr.*, 1905, ii, 804; 1906, ii, 658), whilst Sirkar and Dutta (*Proc.*, 1909, 25, 249; *Zeitsch. anorg. Chem.*, 1910, 67, 225) regard it as arising from the reaction  $\text{Mn}^{\text{IV}} \rightarrow \text{Mn}^{\text{II}} + \text{O}_2$ . The velocity of the latter reaction is, however, very small, whilst the evolution of oxygen is most rapid during, and not after, the reduction of the permanganate by manganous salt or by organic matter.

C. H. D.

**Action of Mixtures of Carbon Monoxide or Carbon Dioxide with Hydrogen on Oxides of Iron.** ARMAND GAUTIER and P. CLAUSEMANN (*Compt. rend.*, 1910, 151, 355—359. Compare *Abstr.*, 1906, ii, 538; this vol., ii, 607, 709).—A mixture of carbon monoxide (3 mols.) and hydrogen (1 mol.) passed over heated magnetic oxide of iron converts it into a mixture of the carbide,  $\text{Fe}_3\text{C}$ , with ferric oxide and free carbon. The product yields methane and hydrogen when heated in a vacuum at  $100^\circ$ . Similar results are obtained when carbon monoxide and hydrogen are passed over freshly-reduced iron at  $1250^\circ$ ; the mixture of gases evolved contains small amounts of methane.

Carbon monoxide and hydrogen saturated with water vapour were passed over iron at  $250$ — $300^\circ$ . The aqueous distillate contained a

trace of formaldehyde, and held in suspension colourless, highly refractive spangles. Extraction with ether resulted in the isolation of a substance resembling vaselin in general properties. After a time it partly solidified, and then had m. p.  $35-36^{\circ}$ ; on heating it evolved a fatty odour.

The bearing of these observations on the formation of petroleum is discussed.

W. O. W.

**Negative Ferric Hydroxide. I. The Preparation and Properties of Negative Ferric Hydroxide.** HERMANN W. FISCHER (*Biochem. Zeitsch.*, 1910, 27, 223-237).—The investigations were undertaken with the view of finding an antidote to arsenic poisoning, such as occurs in treatment with atoxyl and other similar drugs. The colloidal iron hydroxide, as ordinarily prepared, has a positive charge, and as serum proteins are negatively charged, such a preparation when injected can lead to embolisms. If sodium hydroxide be added to ferric chloride solution containing glycerol, at a certain point precipitation takes place, and the solution remains neutral; on further addition of the base, the precipitate redissolves. This "protective" action of glycerol in causing colloidal solution is characteristic of other hydroxyl-containing substances, such as herulose, mannitol, etc., and the author summarises the literature on this subject. The "protection" is probably of chemical nature. The weak basic ferric hydroxide hydrosols form a transparent, ruby-red solution, which can be made to contain a high percentage of metal. On prolonged dialysis, the solution forms a gel, which will liquefy on addition of alkali or "protective" substance. A gel containing only 1% iron is quite firm. The author points to certain analogies in the properties of iron in this form to the iron in hæmoglobin. S. B. S.

**Negative Ferric Hydroxide. II. Ferric Hydroxide and Serum.** HERMANN W. FISCHER (*Biochem. Zeitsch.*, 1910, 27, 238-245).—Positively-charged ferric hydroxide forms precipitates with the negatively-charged serum proteins. The negative, colloidal ferric hydroxide (see preceding abstract) was found to be very toxic to rabbits after intravenous injection. If such hydrosols contain excess of alkali and sufficient amount of "protective" substance, they will not form precipitates with serum, and are not immediately toxic. They act, however, toxically (if intravenously injected) after some hours. A figure is given of an apparatus for rapid dialysis.

S. B. S.

**Chromic Chloride. III. NIELS BJERRUM** (*Zeitsch. physikal. Chem.* 1910, 73, 724-759. Compare Abstr., 1907, ii, 554, 622).—There are two distinct classes of basic chromium compounds, the manifestly basic, which are formed momentarily in aqueous solution at the ordinary temperature, and the latent basic, which are only formed slowly in aqueous solution. The present paper is concerned with the manifestly basic compounds formed from the bluish-violet chromic chloride hexahydrate. The degree of hydrolysis of solutions of the chloride in the presence of varying proportions of alkali was determined with the hydrogen electrode in the usual way.

It is shown that, contrary to the statement of Sand and Grammeling (Abstr., 1908, ii, 293), the chloride itself is unimolecular. On progressive hydrolysis, it gives rise to two soluble, manifestly, basic chlorides,  $\text{Cr}(\text{OH})\text{Cl}_2$  and  $\text{Cr}(\text{OH})_2\text{Cl}$ , and an insoluble, grey-green, manifestly, basic hydroxide. The compound  $\text{Cr}(\text{OH})_2\text{Cl}$  is never present in any large proportion, and the hydroxide is formed only on addition of alkali. The hydroxyl in these compounds is united directly to the chromium atom. The amounts of water associated with the molecules have not been determined, but the respective formulae are probably as follows:  $[\text{Cr}(\text{H}_2\text{O})_5(\text{OH})]\text{Cl}_2$ ;  $[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]\text{Cl}$ ;  $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})_3$ .

The relative amounts of these substances, in solution under varying conditions are given by the following equations:

$$k_1 = \frac{[\text{Cr}(\text{OH})\text{Cl}_2][x]}{[\text{CrCl}_3]}$$

= 0.22 at 0°, 0.62 at 17°, and 0.98 at 25°.

$$k_2 = \frac{[\text{Cr}(\text{OH})_2\text{Cl}][x]}{[\text{Cr}(\text{OH})\text{Cl}_2]}$$

= 0.0025 (in  $N/10$  solution of potassium chloride) at 0° and 0.0059 at 17°.  $k_3 = \text{Cr}(\text{OH})_2\text{Cl} \cdot x^2$  is 36,000 in  $N/10$  potassium chloride solution at 0° and 10,300 at 17°. In the above equations,  $x$  is the concentration of free acid, and the unit of concentration is  $1/10,000$  molar throughout.

From the displacement of the equilibria with temperature, the heats of reaction are calculated in the usual way. The reaction  $\text{Cr}(\text{OH})_3 + 3\text{HCl} = \text{CrCl}_3 + 3\text{H}_2\text{O}$  gives out 21,200 cal., the reaction  $\text{Cr}(\text{OH})_2\text{Cl} + \text{HCl} = \text{Cr}(\text{OH})\text{Cl}_2 + \text{H}_2\text{O}$  at least 8060 cal., and the reactions  $\text{Cr}(\text{OH})\text{Cl}_2 + \text{HCl} = \text{CrCl}_3 + \text{H}_2\text{O}$  gives 9600 cal.

Freshly precipitated chromic hydroxide is a well-defined chemical compound, the solubility product of which is  $4.2 \times 10^{-14}$  at 0° and  $54 \times 10^{-16}$  at 17° in  $1/10,000$  molar units.

G. S.

Complex Metal Ammonias. X. ALFRED WERNER (*Annalen*, 1910, 375, 1—144. Compare Abstr., 1909, ii, 49).—The author's investigations on the complex metal ammonias have now reached such a stage that a summary of the results obtained can be given. Such a summary of the complex cobalt ammonias is given in the present paper, together with the results of hitherto unpublished investigations; there is also a detailed account of the methods used for deducing the constitution of these complex compounds.

The general results arrived at may be briefly summarised as follows:

(A) *Theoretical Results in Connection with Valency.*—(1) The oxygen of an hydroxyl group linked to one cobalt atom can enter into com-

bination with a second cobalt atom, thus:  $\text{Co} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{O} \end{smallmatrix} \text{Co}$ . (2) The

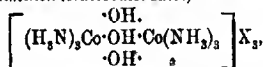
nitrogen of an amino-group can act similarly, thus:  $\text{Co} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{N} \end{smallmatrix} \text{Co}$ . This linking is very stable, and plays the chief part in the formation of complex cobalt ammonias. (3) The oxygen molecule can form the connecting link between two cobalt atoms,  $\text{Co} \cdot \text{O}_2 \cdot \text{Co}$ ; these atoms may be both trivalent (dicobaltic compounds), or the one trivalent and the other quadrivalent (cobalticobalt compounds). (4) In the complex cobalt ammonias two cobalt atoms are never directly linked one with the other. (5) If two cobalt atoms are already linked by the  $\text{OH}$

or  $\cdot\text{NH}_2$  groups, the following atomic groups may also form additional bridged linkings:  $\text{NO}_2$ ;  $\text{SO}_2$ ;  $\text{O}\cdot\text{COMe}$ ;  $\text{O}\cdot\text{COR}$ ;  $\cdot\text{C}_2\text{O}_4$ . (6) Two cobalt atoms may be linked to each other by one, two, or three bridged linkings. The following combinations have been proved to exist: (a) Dicobalt ammonias: (a) with one bridged linking,  $\text{Co}\cdot\overset{\cdot\text{X}}{\text{X}}\cdot\text{Co}$ , where  $\text{X}=\text{NH}_2$  or  $\text{O}_2$ ; ( $\beta$ ) with two bridged linkings,  $\text{Co}\cdot\overset{\cdot\text{X}}{\text{Y}}\cdot\overset{\cdot\text{X}}{\text{Y}}\cdot\text{Co}$ , where  $\text{X}=\cdot\text{OH}$  or  $\cdot\text{NH}_2$ , and  $\text{Y}=\text{OH}$ ,  $\text{NH}_2$ ,  $\text{O}_2$ ,  $\text{NO}_2$ ; also,  $\text{Co}\cdot\overset{\cdot\text{NH}_2}{\text{Y}}\cdot\overset{\cdot\text{NH}_2}{\text{Y}}\cdot\text{Co}$ , where  $\text{Y}=\text{SO}_4$  or  $\text{C}_2\text{O}_4$ ; ( $\gamma$ ) with three bridged linkings,  $\text{Co}\cdot\overset{\cdot\text{OH}}{\text{X}}\cdot\overset{\cdot\text{OH}}{\text{X}}\cdot\overset{\cdot\text{OH}}{\text{X}}\cdot\text{Co}$ , where  $\text{X}=\text{OH}$ ,  $\text{NO}_2$ ,  $\text{O}\cdot\text{COMe}$ , or  $\text{O}_2$ ;  $\text{Co}\cdot\overset{\cdot\text{OH}}{\text{Y}}\cdot\overset{\cdot\text{OH}}{\text{Y}}\cdot\overset{\cdot\text{OH}}{\text{Y}}\cdot\text{Co}$ , where  $\text{Y}=\text{OH}$ ,  $\text{NO}_2$ , or  $\text{O}\cdot\text{COMe}$ ; and  $\text{Co}\cdot\overset{\cdot\text{NO}_2}{\text{Y}}\cdot\overset{\cdot\text{NO}_2}{\text{Y}}\cdot\text{Co}$ . (b) Tricobalt ammonias: (a) with four

bridged linkings,  $\text{Co}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}$ ; ( $\beta$ ) with six bridged linkings,  $\text{Co}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}$ . (c) Tetra-cobalt ammonias with six bridged linkings,  $\text{Co}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}\cdot\overset{\cdot\text{OH}}{\text{OH}}\cdot\overset{\cdot\text{OH}}{\text{Co}}$ .

(7) In all the compounds investigated the maximum co-ordination number of ter- and quadri-valent cobalt is six, as with the simple cobalt ammonias.

(B). *New Results with Respect to Inorganic Isomerism*.—Three kinds of isomerism are distinguished: (1) *Polymerism or nuclear-polymerism*; for example, *hexamminetrioldicobalt*-salts,



and *dodeca-amminhexolistracobalt*-salts,  $\left[ \text{Co} \left( \overset{\cdot\text{OH}}{\text{OH}} \cdot \text{Co}(\text{NH}_3)_4 \right)_2 \right] \text{X}_6$ .

(2) *Valency isomerism*; for example, *tetraethylenediamine- $\mu$ -aminoperoxo-cobalticobalt* salts,  $\left[ \text{en}_2\text{Co} \begin{array}{c} \text{O}_2 \\ \text{NH}_2 \end{array} \text{Co en}_2 \right] \text{X}_4$ , and *tetraethylenediamine-*

*$\mu$ -ammoniumperoxocobalticobalt* salts,  $\left[ \text{en}_2\text{Co} \begin{array}{c} \text{O}_2 \\ \text{NH} \end{array} \text{Co en}_2 \right] \text{X}_4 \cdot \text{HX}$ .

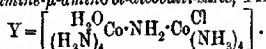
The salts of the former series are green and of neutral reaction, those of the latter being red and of acid reaction. (3) *Co-ordinative position-isomerism*, which may be compared with the organic isomerism:  $\text{CH}_3\cdot\text{CHX}_2$  and  $\text{CH}_2\text{X}\cdot\text{CH}_2\text{X}$ ; for example, symmetrical and asymmetrical *dichlorohexammine- $\mu$ -aminoperoxo-cobalticobalt chloride*,  $\left[ \begin{array}{c} \text{Cl} \quad \cdot\text{NH}_2 \quad \text{Cl} \\ (\text{H}_3\text{N})_3\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_3 \end{array} \right] \text{Cl}_2$  and  $\left[ (\text{H}_3\text{N})_4\text{Co}\cdot\overset{\cdot\text{NH}_2}{\text{O}_2}\cdot\overset{\cdot\text{NH}_2}{\text{Co}}(\text{NH}_3)_2 \right] \text{Cl}_2$ .

Both series of salts are green and resemble each other in appearance, but chemically they are very different.

*Decammine-μ-aminodicobalti-salts*,  $[(H_2N)_5Co \cdot NH_2 \cdot Co(NH_3)_5]X_6$  (compare Abstr., 1909, ii, 49). A new method of preparation is given. When a freshly prepared solution of chloroaquo-octammine-μ-aminodicobalti-chloride is treated with concentrated nitric acid a grey, ish-violet precipitate of *chloronitrate-octammine-μ-aminodicobalti-nitrate*,  $[(H_2N)_4Co \cdot NH_2 \cdot Co \overset{NO_2}{\underset{(NH_3)_4}{\text{N}}}] (NO_3)_2$ , separates. The dry salt is dissolved in liquid ammonia, and, after evaporating off the ammonia, the residue is covered with water and heated on the water-bath until the greater part has dissolved. The insoluble part is filtered from the hot solution and recrystallised from water containing acetic acid, when long, bluish-red needles of *decammine-μ-aminodicobalti-nitrate* are obtained.

[With FRANZ SALZER].—The following compounds derived from the octammine-μ-amino-ol-dicobalti-salts (compare Abstr., 1908, ii, 42) are described.

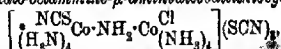
*Chloroaquo-octammine-μ-amino-ol-dicobalti-salts*,  $YX_4$ , where



To prepare the *chloride*,  $YCl_4 \cdot 4H_2O$ , 10 grams of crude sulphato-octammine-μ-aminodicobalti-nitrate (Abstr., 1908, ii, 42) are covered with 150 c.c. of hydrochloric acid ( $D = 1.19$ ) and kept at room temperature, the mixture being well shaken at intervals. The sulphato-nitrate dissolves, the OH bridged linking being destroyed, and then crystals of the chloride are deposited. After twenty-four hours they are collected, dissolved in cold water, and re-precipitated by concentrated hydrochloric acid; brownish-violet needles, readily soluble in water, giving an acid solution. The concentrated solution deposits, after a time, prismatic, reddish-brown crystals of *octammine-μ-amino-ol-dicobalti-chloride*,  $[(H_2N)_4Co \cdot NH_2 \cdot Co \overset{NH_2}{\underset{OH}{\text{N}}} (NH_3)_4] Cl_4 + HCl$ .

On long boiling with concentrated hydrochloric acid the chloride ( $YCl_4$ ) is decomposed completely into pentammine- and tetrammine-cobalti-salts. The freshly prepared aqueous solution gives characteristic precipitates with solutions of chloroplatinic acid, mercuric chloride, and potassium iodide. Dilute sulphuric acid produces a quantitative precipitation of the *sulphate*,  $Y(SO_4)_2 \cdot H_2O$ ; pale reddish-violet crystals. Sodium dithionate gives a voluminous, greyish-violet, crystalline precipitate of the *dithionate*,  $Y(S_2O_8)_2$ .

*Chlorothiocyanato-octammine-μ-aminodicobalthiocyanate*,

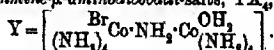


is obtained as a brownish-red, crystalline precipitate when a saturated solution of the corresponding chloride is treated with a saturated solution of ammonium thiocyanate.\* *Chloronitrate octammine-μ-amino-dicobaltinitrate*,  $[(H_2N)_4Co \cdot NH_2 \cdot Co \overset{NO_2}{\underset{(NH_3)_4}{\text{N}}}] (NO_3)_2$ , is prepared by dissolving 3 grams of chloroaquo-octammine-μ-aminodicobalti-chloride in 50 c.c. of ice-cold water, filtering, and adding 15 c.c. of concentrated



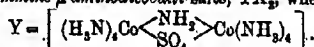
nitric acid. A reddish-violet precipitate is produced, which rapidly changes to a brownish-violet colour. The fresh solution gives no precipitate with silver nitrate at first, but on standing silver chloride is formed. From the warm solution, dilute sulphuric acid precipitates octammine- $\mu$ -amino-ol-dicobalti-sulphate.

*Bromoquo-octammine- $\mu$ -aminodicobalti-salts,  $YX_n$ , where*



To obtain the *bromide*,  $YBr_2$ , octammine- $\mu$ -amino-ol-dicobalti-sulphate (Abstr., 1908, ii, 42) is triturated with concentrated hydrobromic acid. The resulting product is washed free from acid with alcohol, dissolved in ice-cold water, the solution filtered, and then precipitated with concentrated hydrobromic acid; dark brown, flat needles. The aqueous solution is acid, and after a time deposits red, prismatic crystals of octammine- $\mu$ -amino-ol-dicobalti-bromide. The *sulphate*,  $Y(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ , is prepared by adding a freshly prepared solution of the bromide in ice-cold water to dilute sulphuric acid; dark brown crystals, almost insoluble in water.

*Sulphato-octammine- $\mu$ -aminodicobalti-salts,  $YX_n$ , where*



The salts of this series were formerly described as *hydrosulphatoimido-octamminedicobalti-salts* (Abstr., 1898, ii, 224). The best method of preparation is now found to be as follows:—Solutions of pure octammine- $\mu$ -amino-ol salts are heated with sulphuric acid. The pale red sulphate is first precipitated, and dissolves again to a reddish-violet solution, from which the required salts can be precipitated by suitable reagents. The *acid sulphate*,  $Y(\text{SO}_4)(\text{HSO}_4)$ , results when 3 grams of octammine- $\mu$ -amino-ol-dicobalti-chloride are heated with 10 c.c. of water and 2 c.c. of concentrated sulphuric acid until a clear violet solution is obtained. Purplish-violet, prismatic leaflets separate on cooling. The *bromide*,  $YBr_2 \cdot \text{H}_2\text{O}$ , and *nitrate*,  $Y(\text{NO}_3)_2$ , result when concentrated hydrobromic acid and nitric acid respectively are added to a solution of the sulphate. The nitrate forms violet-red crystals.

[With FRANZ SALZER and M. PREPER.]—*Octammine- $\mu$ -aminonitrodi-cobalti-salts,  $YX_n$ , where*  $Y = \left[ (\text{H}_2\text{N})_4 \text{Co} \begin{array}{c} \text{NH}_2 \\ \text{NO}_2 \end{array} \text{Co} (\text{NH}_3)_4 \right]$ . The

nitrate, chloride, and sulphate have previously been described as *hydronitritoimido-octamminedicobalti-salts* (Abstr., 1898, ii, 223), but since then their constitution has been fully investigated. The salts are amongst the most stable of the complex cobalt ammonias. The nitrate,  $Y(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , is the most convenient starting point for the preparation of the other salts. New methods of preparation are as follows: (1) A concentrated solution of sodium nitrite is added drop by drop to a mixture of the green octammine- $\mu$ -aminoperoxocobalticohalate nitrate with excess of concentrated nitric acid. The green nitrate changes to orange-yellow crystals, which are collected and recrystallised from water containing nitric acid. (2) Sodium nitrite is added to a warm concentrated aqueous solution of octammine- $\mu$ -amino-ol-dicobalti-chloride until a yellowish-brown colour is obtained. The nitrate separates on cooling, after the addition of nitric acid. (3) A con-

concentrated, fresh solution of chloroaquo-octammine- $\mu$ -aminodicobaltichloride is treated with sodium nitrite and warmed until the colour becomes orange. The addition of concentrated nitric acid then gives a precipitate of the required nitrate.

With ammonia the nitrate,  $Y(NO_3)_4$ , does not lose one molecule of acid with the formation of imino-salts. From a solution containing pyridine, it crystallises with one molecule of pyridine, the base not being contained in the complex. Besides the chloride,  $YCl_4 \cdot H_2O$  (*loc. cit.*), there is also a *chloride*,  $YCl_4 \cdot 4H_2O$ , which is obtained when the ordinary chloride is crystallised from a solution containing pyridine. The *bromide*,  $YBr_4 \cdot 3H_2O$ , is obtained by treating a solution of the sulphate with the calculated quantity of barium bromide, and precipitating the filtrate from the barium sulphate with hydrobromic acid; brownish-red, rhombic prisms or plates. The *iodide*,  $YI_4 \cdot H_2O$ , is obtained from the nitrate by precipitation with potassium iodide; large, dark red prisms. When recrystallised from water containing pyridine it contains  $4H_2O$ .

[With ADOLF GRÜN.]—Octammine- $\mu$ -aminoparaoxocobalticobalt salts,  $YX_4$ , where  $Y = \left[ (H_2N)_4Co \begin{smallmatrix} III \\ \searrow \\ NH_2 \\ \nearrow \\ O \end{smallmatrix} Co \begin{smallmatrix} IV \\ \nearrow \\ NH_2 \\ \searrow \\ O \end{smallmatrix} (NH_3)_4 \right]$ . These were formerly described as oxodi-imido-octamminedicobaltic-salts (Abstr., 1898, ii, 223), but further investigation has shown them to have the constitution given above. Reducing agents, such as hydriodic acid, give octammine- $\mu$ -amino-di-cobaltic-salts. When warmed with concentrated sulphuric acid, one and a-half atoms of oxygen are liberated for every two atoms of cobalt, corresponding with the change from quadri- to ter-valent cobalt. On further strongly heating, one-third atom of nitrogen is evolved for each atom of cobalt, corresponding with the change from ter- to bi-valent cobalt.

The *nitrate*,  $YX_4$ , is obtained by treating the green sulphate contained in Vortmann's sulphate (Abstr., 1908, ii, 42) with nitric acid; it forms dark green, prismatic crystals, which are anhydrous. A hydrated nitrate could not be obtained (compare Abstr., 1908, ii, 223). The aqueous solution rapidly decomposes, cobalt oxide being deposited. The *sulphate*,  $Y(SO_4)_2 \cdot 2H_2O$ , is precipitated when aqueous solutions of other salts are treated with dilute sulphuric acid; greenish-grey, prismatic crystals. The *chloride*,  $YCl_4 \cdot H_2O$ , and the *bromide*,  $YBr_4 \cdot H_2O$ , are obtained by triturating the sulphate with concentrated hydrochloric and hydrobromic acids respectively, and forms dark green crystals. Sodium dithionate precipitates the *dithionate*,  $Y(S_2O_6)_2$ , from an aqueous solution of the nitrate containing acetic acid.

The central group,  $Co \begin{smallmatrix} \nearrow \\ NH_2 \\ \searrow \\ O \end{smallmatrix} Co$ , of this series is very stable. By warming the nitrate with 10% ethylenediamine all the ammonia molecules can be replaced by ethylenediamine. If the resulting solution is then neutralised with nitric acid at the ordinary temperature, a green salt is obtained; when the neutralisation is carried out at low temperatures a red salt is obtained. These salts only differ in their molecular composition, in that the former is anhydrous, whereas the latter contains 2 mols. of water of crystallisation. The aqueous solution of the former is neutral, whereas that of the latter is acid. On

warming a nitric acid solution of the red salt, it changes into the green salt. The green salt is *tetraethylenediamine-μ-aminoperoxocobalticobalt nitrate*,  $Y(NO_3)_3$ , where  $Y = \left[ en_2Co \begin{smallmatrix} \text{NH}_2 \\ \text{O}_2 \end{smallmatrix} Co en_2 \right]$ . During the preparation some decomposition also takes place, with the formation of *triethylenediaminecobalti*-salts. Reduction of the nitrate with sodium iodide or potassium thiocyanate gives precipitates of the corresponding tetraethylenediamine-μ-amino-ol-dicobalti-iodide and thiocyanate. The *bromide*,  $YBr_3 \cdot 5H_2O$ , is precipitated as yellowish-green crystals when ammonium bromide is added to a cold saturated solution of the nitrate.

The red salt is *tetraethylenediamine-μ-ammoniumperoxocobalticobalt nitrate*,  $[Y \cdot HNO_3](NO_3)_3 \cdot 2H_2O$ , where  $Y = \left[ en_2Co \begin{smallmatrix} \text{O}_2 \\ \text{NH} \end{smallmatrix} Co en_2 \right]$ .

The *bromide*,  $[Y \cdot HBr]Br_3 \cdot 3H_2O$ , obtained by precipitating a solution of the red nitrate with potassium bromide, forms red crystals giving a brown solution in water, which is first turned red and then green by mineral acids. A bromide containing  $1H_2O$  can also be obtained.

Under the action of ammonia both the green and the red salts lose a molecule of acid, forming *tetraethylenediamine-μ-iminoperoxocobalticobalt* salts. The *iodide*,  $\left[ en_2Co \begin{smallmatrix} \text{NH} \\ \text{O}_2 \end{smallmatrix} Co en_2 \right] I_3 \cdot 5H_2O$ , is readily

obtained from tetraethylenediamine-μ-aminoperoxocobalticobalt bromide by triturating the mixture with ammonia and sodium iodide. It is purified by solution in water and re-precipitation with potassium iodide; small, brown needles. On shaking the aqueous solution with silver chloride, a solution of the *chloride* results, but crystals cannot be obtained. If hydrochloric acid is added to this solution, it first becomes red, the ammoniumperoxo-salt being formed, and then green, isomerisation to the aminoperoxo-salt taking place. The solution of the iodide gives characteristic precipitates with potassium platinochloride and with potassium aurichloride. Silver nitrate first gives a precipitate of silver iodide, and then an *additive compound* of the nitrate with silver nitrate,  $3 \left[ en_2Co \begin{smallmatrix} \text{O}_2 \\ \text{NH} \end{smallmatrix} Co en_2 \right] (NO_3)_3 + 5AgNO_3$ ; dark brown crystals. Similar addition compounds may be obtained with copper nitrate (apple-green crystals) and with mercuric chloride (brilliant red crystals).

Both the red and the green salts give rise to *tetraethylenediamine-μ-amino-ol-dicobalti*-salts when reduced by means of acetic acid and potassium iodide. The *iodide*,  $YI_4$ , where  $Y = \left[ en_2Co \begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix} Co en_2 \right]$ , is readily obtained from the aminoperoxodicobalt nitrate in this way. The periodide which is first formed is destroyed with sodium thio-sulphate, and the iodide separates as light red crystals from the resulting solution. The *bromide*,  $YBr_4 \cdot 4H_2O$ , may be obtained by adding ammonium bromide to the solution of the iodide; dark red crystals.

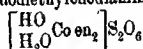
When an aqueous solution of tetraethylenediamine-μ-aminoperoxodicobalt nitrate is treated with glacial acetic acid and excess of potassium thiocyanate, red crystals of the thiocyanato are obtained.

If these are oxidised with concentrated nitric acid, the resulting solution precipitated with alcohol, and ammonium bromide added to an aqueous solution of the precipitate, red crystals of *sulphato-tetraethylenediamine-μ-aminodibalt-bromide*,  $\left[ \text{en}_2\text{Co} \begin{smallmatrix} \text{NH}_2 \\ \text{SO}_4 \end{smallmatrix} \text{Co en}_2 \right] \text{Br}_2$ , are obtained.

[With E. KINDSCHER.]—*Octammine-dioldibalt-salts*,  $\text{YX}_4$ , where  $\text{Y} = \left[ (\text{H}_3\text{N})_4\text{Co} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \text{Co}(\text{NH}_3)_4 \right] \text{X}_4$ . The chloride, bromide, nitrate, thiocyanate, dithionate, and sulphate of this series have been described previously (Abstr., 1907, ii, 965). The following salts have all been prepared from an aqueous solution of the chloride by double decomposition with soluble alkali salts of the various acids. *Iodide*,  $\text{YI}_4 \cdot 2\text{H}_2\text{O}$ , dark violet crystals; *chlorate*,  $\text{Y}(\text{ClO}_3)_4$ , crimson crystals; *bromate*,  $\text{Y}(\text{BrO}_3)_4$ , ruby-red crystals; *iodate*,  $\text{Y}(\text{IO}_3)_4$ , bright violet crystals; *oxalate*,  $\text{Y}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , ruby-red crystals; *chromate*,  $\text{Y}(\text{CrO}_4)_2$ , light brown, earthy precipitate; *phosphate*,  $\text{Y}(\text{HPO}_4)_2 \cdot 6\text{H}_2\text{O}$ , rose-red crystals; *platinochloride*,  $\text{Y}(\text{PtCl}_4)_2$ , red crystals; *platinichloride*,  $\text{Y}(\text{PtCl}_4)_2 \cdot 6\text{H}_2\text{O}$ ,

copper-red needles; *aurichloride*,  $\text{Y}(\text{AuCl}_4)_2 \cdot 4\text{H}_2\text{O}$ , red crystals; *silicofluoride*,  $\text{Y}(\text{SiF}_6)_2$ , light violet precipitate.

[With Jos. RAPAPORT.]—*Tetraethylenediamine-diol-dibalt-salts*,  $\text{YX}_4$ , where  $\text{Y} = \left[ \text{en}_2\text{Co} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \text{Co en}_2 \right]$ . The salts of this series were prepared from *cis*-hydroxo-aquodithylenediaminecobaltidithionate,



(Abstr., 1907, i, 189), for which a new method of preparation from hexaethylenediaminehexoltetracobalt-nitrate (Abstr., 1907, i, 482) is given. By the action of concentrated hydrochloric acid on the hexol-nitrate, crystals of *cis*-diaquodithylenediaminecobalt chloride are obtained. On treating an aqueous solution of these crystals with pyridine and sodium dithionate, crystals of the *cis*-hydroxo-aquodithylenediaminecobaltidithionate are readily formed. When this compound is heated to constant weight at 100–110°, water is lost, with the formation of *tetraethylenediamine-diol-dicobaltidithionate*,  $\text{Y}(\text{S}_2\text{O}_6)_2$ . The *bromide*,  $\text{YBr}_4 \cdot 4\text{H}_2\text{O}$ , may be obtained from the dithionate by triturating with ammonium bromide and water, and forms reddish-violet needles, which lose  $2\text{H}_2\text{O}$  at 100°, or on keeping over concentrated sulphuric acid. The *thiocyanate*,  $\text{Y}(\text{SCN})_4 \cdot 3\text{H}_2\text{O}$ , forms a purple, crystalline precipitate when potassium thiocyanate is added to a solution of the bromide. Under similar conditions, sodium nitrate gives purple crystals of the *nitrate*,  $\text{Y}(\text{NO}_3)_4$ .

Both the octammine- and the tetraethylenediamine-diol-dibalt-salts are readily decomposed by concentrated hydrochloric or hydrobromic acids, giving rise to a mixture of *cis*-diaquo- and *cis*-dichloro-salts. This reaction is of use in determining the configuration of stereo-isomeric cobalt ammonias.

In the preparation of *cis*-dichlorotetraminecobalt-chloride (violet-chloride,  $[\text{Cl}_2\text{Co}(\text{NH}_3)_4]\text{Cl}$ ) from octammine-diol-dibalt-chloride, the crude substance sometimes assumes a superficial red colour when dried

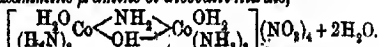
over phosphoric oxide. The conditions governing this change are not known; but if the partly changed salt is dissolved in water and sodium dithionate added after half an hour, orange-yellow crystals of octammine- $\mu$ -diaminodicobaltidithionate,  $Y(S_2O_4)_2$ , where



are precipitated. On rubbing these crystals with ammonium bromide and a little water, red crystals of the bromide,  $YBr_2 \cdot 4H_2O$ , are obtained.

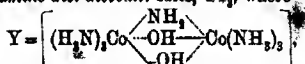
[With J. FÜRSTENBERG.]—Melanochloride (Abstr., 1898, ii, 226) was used as the starting point for the following series of salts. A new and quicker method of preparation of this chloride is described. A mixture of 650 grams of cobalt chloride with 400 c.c. of water and 2 litres of 25% ammonia is heated to boiling, filtered from the precipitated cobalt oxide, and exposed to the air for forty-eight hours. The resulting brownish-red solution is filtered from the crystals which have deposited, and mixed with 3 litres of concentrated hydrochloric acid. The resulting brownish-red precipitate is quickly collected and extracted with cold water until it becomes pure grey in colour and the wash water is coloured a brownish-violet. One kilo. of cobalt chloride gives about 60 grams of melanochloride.

*Diaguehexammine- $\mu$ -amino-ol-dicobalt-nitrate*,



Twenty grams of melanochloride are triturated with a slightly acid solution of 36 grams of silver nitrate in 60 c.c. of water, and the mixture heated to 50° for some time. The silver chloride is collected and heated at 80° with separate quantities of 60 c.c. of very weak nitric acid until it is colourless. To the united red extracts is added alcohol until incipient crystallisation; on cooling in a freezing mixture, red crystals of the nitrate separate. After solution in water and re-precipitation with concentrated nitric acid, garnet-red, flat, quadratic prisms are obtained. The aqueous solution is acid.

*Hexammine- $\mu$ -amino-diol-dicobalt-salts*,  $YI_2$ , where

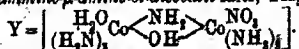


give neutral aqueous solutions. The *iodide*,  $YI_2$ , is precipitated by the addition of solid potassium iodide to a solution of diaguehexammine- $\mu$ -amino-ol-dicobalt-nitrate; brownish-red needles. The *bromide*,  $YBr_2 \cdot 2H_2O$ , results when ammonium bromide is used instead of potassium iodide; it may also be obtained from the chloride by treatment with silver bromide; dark red needles. The *chloride*,



is prepared from the iodide or bromide by means of silver chloride; bright red needles. The *nitrate*,  $Y(NO_3)_2 \cdot 2H_2O$ , results from the interaction of the iodide and silver nitrate; small red crystals.

*Nitratodiaguehexammine- $\mu$ -amino-ol-dicobalt-salts*,  $YX_2$ , where

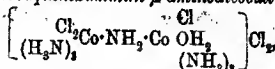


The *nitrate*,  $Y(NO_3)_2 \cdot 2H_2O$  (compare Abstr., 1899, ii, 658), is best

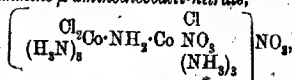
prepared as follows: One gram of diaquohexammine- $\mu$ -amino-ol-dicobalti-nitrate is dissolved in 7 c.c. of hot water to which a few drops of nitric acid have been added. To the cooled solution, 18 c.c. of concentrated nitric acid are added; after a few minutes, yellowish-brown, flat needles of the required nitratonitrate separate. The addition of concentrated hydrochloric acid to a cold solution of the nitrate precipitates yellowish-brown, flat needles of the *chloride*,  $\text{YCl}_2 \cdot \text{H}_2\text{O}$ . With hydrobromic acid or ammonium bromide, flesh-coloured, flat needles of the *bromide*,  $\text{YBr}_2 \cdot \text{H}_2\text{O}$ , are obtained.

[With FRL. SIGNE MALMGREN].—When nitratoaquohexammine- $\mu$ -amino-ol-dicobalti-nitrate is dissolved in liquid ammonia and the ammonia allowed to evaporate, a reddish-brown residue is obtained. If this is extracted with cold water and ammonium sulphate added to the extracts, an insoluble sulphate is precipitated, from which a soluble nitrate may be obtained by treatment with ammonium nitrate. The solution of the nitrate gives, with ammonium bromide a red precipitate of octammine- $\mu$ -amino-ol-dicobalti-bromide. This reaction proves the presence of a  $\mu$ -amino-bridged linking in the hexamine compound.

[With J. FÜRSTENBERG].—On adding concentrated hydrochloric acid to a warm solution of diaquohexammine- $\mu$ -amino-ol-dicobalti-nitrate, microscopic, dark violet, hexagonal leaflets are precipitated. When dried at 60–65°, it consists of tetrachlorohexammine- $\mu$ -aminodicobalti-chloride,  $\left[ \begin{array}{c} \text{Cl}_2 \\ (\text{H}_2\text{N})_3 \end{array} \text{Co} \cdot \text{NH}_2 \cdot \text{Co} \begin{array}{c} \text{Cl}_2 \\ (\text{NH}_2)_3 \end{array} \right] \text{Cl}$ . When dried at the ordinary temperature only three of the chlorine atoms are non-ionic, the salt then being trichloroaquohexammine- $\mu$ -aminodicobalti-chloride,



that is, the pure melanochloride. When this salt is triturated with concentrated nitric acid, dissolved in cold water, and the solution immediately precipitated with nitric acid, violet-black crystals of trichloronitratoaquohexammine- $\mu$ -aminodicobalti-nitrate,



are obtained.

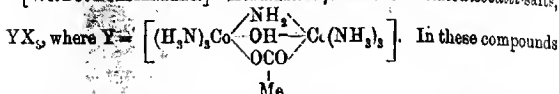
Tetrabromohexammine- $\mu$ -aminodicobalti-salts,  $\text{YX}$ , where  $\text{Y} = \left[ \begin{array}{c} \text{Br}_2 \\ (\text{H}_2\text{N})_3 \end{array} \text{Co} \cdot \text{NH}_2 \cdot \text{Co} \begin{array}{c} \text{Br}_2 \\ (\text{NH}_2)_3 \end{array} \right]$ . The bromide,  $\text{YBr}_2 \cdot 2\text{H}_2\text{O}$ , is formed on warming the aqueous solution of hexamine- $\mu$ -amino-diol-dicobalti-bromide with concentrated hydrobromic acid; brownish-yellow, crystalline powder, which becomes anhydrous at 70–80°. The nitrate,  $\text{YNO}_3 \cdot 2\text{H}_2\text{O}$ , resembles the bromide in appearance, and is prepared from the latter by trituration with nitric acid.

The salts of the trichloro-, tetrachloro-, and tetrabromo-series are all re-converted into tetraquohexamminedicobalti-nitrate by digestion with a slightly acid solution of silver nitrate.

Dichlorohexammine- $\mu$ -aminonitrodicobalti-salts,  $\text{YX}_2$ , where  $\text{Y} = \left[ \begin{array}{c} \text{Cl} \\ (\text{H}_2\text{N})_3 \end{array} \text{Co} \begin{array}{c} \text{NH}_2 \\ \text{NO}_2 \end{array} \text{Co} \begin{array}{c} \text{Cl} \\ (\text{NH}_2)_3 \end{array} \right]$ . In these compounds the nitro-

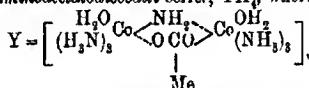
group\* is very firmly combined. The *chloride*,  $\text{YCl}_3 \cdot \text{H}_2\text{O}$ , is obtained by warming 1 gram of tetraquohexammine- $\mu$ -amino-ol-nitrate with 0.25 gram of sodium nitrite and a little water. To the resulting orange-coloured solution, concentrated hydrochloric acid is added, when nitrous fumes are evolved and the chloride deposited as red flakes. It is identical with the hydronitritoimidohexamminedicobalti-chloride previously prepared from melanochloride (Abstr., 1898, ii, 226). The *nitrate*,  $\text{Y}(\text{NO}_3)_3$ , is prepared by triturating the chloride with concentrated nitric acid; reddish-brown, crystalline powder.

[With J. FÜRSTENBERG.]—*Hexammine- $\mu$ -amino-ol-acetatodicobalti-salts*,



the acetic acid residue is very firmly combined. Their properties are very different from the nl-compounds, from which they are derived, as they no longer show the so-called melano-reaction. Their aqueous solutions are neutral. The *iodide*,  $\text{YI}_3$ , is prepared by warming a solution of diaquohexammine- $\mu$ -amino-ol-dicobalti-nitrate with acetic acid, and then adding excess of potassium iodide. On cooling, it is deposited as vivid red, prismatic needles or plates. The *bromide*,  $\text{YBr}_3$ , and the *chloride*,  $\text{YCl}_3$ , are obtained from the iodide by treatment with silver bromide and chloride respectively; bright red needles. The *nitrate*,  $\text{Y}(\text{NO}_3)_3$ , results from the interaction of the iodide and silver nitrate. With potassium platinochloride, the solution of the chloride gives bright red crystals of the *platinochloride*,  $\text{Y}_2(\text{PtCl}_6)_3$ .

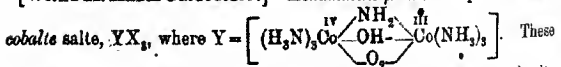
When solutions of these salts are precipitated with nitric acid they do not give the corresponding nitrate, but the nitrate of the *diaquohexammine- $\mu$ -aminoacetatodicobalti-series*,  $\text{YX}_3$ , where



the nitric acid breaking one of the nl-linkings.

The *nitrate*,  $\text{Y}(\text{NO}_3)_3$ , is best prepared by warming a solution of hexammine- $\mu$ -amino-diol-dicobalti-nitrate with acetic acid at  $70^\circ$ , and then adding concentrated nitric acid to the cooled solution; bright red leaflets, with acid reaction. The *bromide*,  $\text{YBr}_3$ , is precipitated from a solution of the nitrate on the addition of 40% hydrobromic acid; red crystals.

[With FEL. MARIE GRIGOSIEFF.]—*Hexammine- $\mu$ -amino-ol-peroxocobalti-*



salts belong to the same series as the oxoimidohexamminedicobalti-salts (Abstr., 1899, ii, 658). The starting point is a black chloride, obtained by the action of silver nitrate on melanochloride (see diaquohexammine- $\mu$ -amino-nl-dicobalti-nitrate). The filtrate from the silver chloride,

after the addition of a little ammonium nitrate, is kept for a quarter of an hour. The resulting crystals are collected, and the filtrate mixed with concentrated hydrochloric acid and warmed at  $40^{\circ}$ . The black chloride then separates; it contains one chlorine atom less and two atoms of oxygen more than melanochloride. To prepare the *bromide*,  $YBr_2 \cdot 2H_2O$ , the black chloride is triturated with a concentrated solution of silver nitrate; the filtrate from the silver chloride gives dark green crystals of the bromide on saturation with ammonium bromide. The *chloride*,  $YCl_2 \cdot H_2O$ , results from the interaction of the bromide and silver chloride, and the *nitrate*,  $Y(NO_3)_2 \cdot H_2O$ , from the double decomposition of the bromide and silver nitrate. The latter forms dark green scales.

The above series of salts also result from the degradation of the octammine- $\mu$ -aminoperoxocobalticobalte salts; aqueous solutions of the latter are heated with ammonium chloride, and the reaction mixture saturated with hydrogen chloride, when the hexammine chloride separates. Also, on reduction with potassium iodide and acetic acid they give rise to hexammine- $\mu$ -amino-diol-dicobalti-salts.

When an aqueous solution of hexammine- $\mu$ -amino-ol-peroxocobalticobalte chloride is warmed with concentrated hydrochloric acid, small, black crystals of *s-dichlorohexammine- $\mu$ -aminoperoxocobalticobalte chlor*  $le$ ,  $YCl_2$ , where  $Y = \left[ \begin{array}{c} Cl \\ (H_3N)_3Co < \begin{array}{c} NH_2 \\ O_2 \end{array} > Co \begin{array}{c} Cl \\ (NH_3)_3 \end{array} \end{array} \right]$ , separate.

The *nitrate*,  $Y(NO_3)_2$ , resembles the chloride in appearance, and is obtained from the latter by trituration with concentrated nitric acid. From the corresponding hexammine bromide and hydrobromic acid, small, greenish-black crystals of *s-dibromohexammine- $\mu$ -amino-*

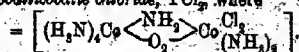
*peroxocobalticobalte bromide*,  $\left[ \begin{array}{c} Br \\ (H_3N)_3Co < \begin{array}{c} NH_2 \\ O_2 \end{array} > Co \begin{array}{c} Br \\ (NH_3)_3 \end{array} \end{array} \right] Br_2$  are obtained. The action of liquid ammonia on this bromide gives rise to octammine- $\mu$ -aminoperoxocobalticobalte bromide, thus proving that the above octammine- and hexammine-peroxo-salts both contain the same nucleus,  $\begin{array}{c} III \\ Co < \begin{array}{c} NH_2 \\ O_2 \end{array} > IV \end{array}$ .

Reduction of hexammine- $\mu$ -aminoperoxo-ol-cobalticobalte bromide with sulphurous acid and addition of concentrated hydrobromic acid to the resulting solution gives greenish-black crystals of tetrabromohexammine- $\mu$ -aminodicobalti-bromide (q.v.), which with silver nitrate in dilute nitric acid solution gives diaquohexammine- $\mu$ -amino-ol-dicobaltioitrate.

When solutions of octammine- $\mu$ -aminoperoxocobalticobalte nitrate are heated with excess of ammonium carbonate instead of ammonium chloride, and the cold reaction mixture then treated with hydrochloric acid, dark olive-green crystals of a chloride are obtained, which is isomeric with the symmetrical dichloro-chloride just described. It is readily soluble in water, however, whereas the symmetrical chloride is sparingly soluble. It contains the nucleus  $\begin{array}{c} II \\ Co < \begin{array}{c} NH_2 \\ O_2 \end{array} > II \end{array}$ , since liquid ammonia transforms it again into the octammine- $\mu$ -aminoperoxo-ol-cobalticobalte salt, and therefore differs from the symmetrical chloride only in the

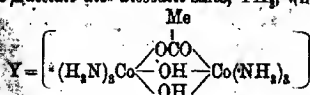


position of the ammonia molecules. It is *α*-dichlorohexammine-*μ*-aminoperacobalticobaltic chloride,  $YCl_2$ , where



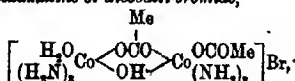
On heating with dilute hydrochloric acid, it is decomposed, with the formation of chloropentamminecobaltic chloride. The *bromide*,  $YBr_2$ , is obtained by saturating a solution of the chloride with ammonium bromide; small, glistening, dark brown needles.

*Hexammine-μ-acetato-diol-dicobalt* salts,  $YX_2$ , where



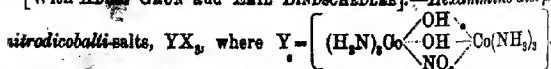
These salts are derived from the hexamminetrioldicobalt-salts, the preparation and constitution of which have been previously described (Abstr., 1908, ii, 43). The *chloride*,  $YCl_2 \cdot 4H_2O$ , is prepared by evaporating a concentrated aqueous solution of hexamminetrioldicobaltic chloride on the water-bath with glacial acetic acid; long, red needles;  $3H_2O$  are lost at  $100-110^\circ$ . The *bromide*,  $YBr_2 \cdot H_2O$ , is prepared in a similar way from the corresponding triol-bromide; violet-red prisms, which become anhydrous at  $110^\circ$ . It dissolves in saturated hydrochloric acid at  $0^\circ$ ; and the blue solution then deposits crystals of trichlorotriammine cobalt,  $(H_2N)_3CoCl_3$  (compare Abstr., 1906, ii, 760). The *iodide*,  $YI_2 \cdot H_2O$ , and the *thiocyanate*,  $Y(SCN)_2 \cdot H_2O$ , are precipitated when a solution of the bromide is saturated with potassium iodide and thiocyanate respectively; red plates and slender, red crystals. The *nitrate*,  $Y(NO_3)_2 \cdot 2H_2O$ , is prepared from the hexamminetriolnitrate by evaporation with glacial acetic acid; shining red, monoclinic prisms, which lose  $1H_2O$  at  $100-110^\circ$ . The *bromide dithionate*,  $YBr(S_2O_8) \cdot H_2O$ , forms as a red, crystalline precipitate when sodium dithionate is added to a concentrated solution of diacetato-diaquohexamminedicobaltic-bromide.

*Diacetatoaqueohexammine-ol-dicobaltic-bromide*,



is obtained in red needles when a saturated solution of hexamminetriol-dicobaltic-bromide is mixed with half its volume of glacial acetic acid and the solution evaporated to half its original volume on the water-bath. It is very unstable in aqueous solution, salts of the metals always giving precipitates of the hexammine-*μ*-acetato-diol-dicobaltic-series.

[With ADOLF GRÜX and EMIL BINDSCHEDLER].—*Hexammine-diol-μ*-nitrodicobaltic-salts,  $YX_2$ , where  $Y =$

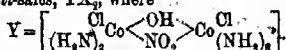


These salts are formed by the action of nitrous acid on the hexamminetrioldicobaltic-salts in acetic-acid-aqueous solution. They are deep orange in colour, and the nitro-group is very firmly combined.

On warming with hydrochloric or hydrobromic acid, an ol-linking is broken, two halogen atoms entering into the complex radicle.

The *chloride*,  $\text{YCl}_2 \cdot \text{H}_2\text{O}$ , is formed from the hexamminetriol chloride in the way indicated, and precipitated from solution by the addition of concentrated hydrochloric acid; felted, orange-red needles. The *bromide*,  $\text{YBr}_2 \cdot \text{H}_2\text{O}$ , forms orange-red, felted leaflets. The *nitrate*,  $\text{Y}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , is precipitated in orange-red, rhombic plates on adding nitric acid to a solution of the chloride. Sodium sulphate precipitates the *sulphate*,  $\text{Y}_2(\text{SO}_4)_3$ , in orange-red, rhombic, prismatic crystals.

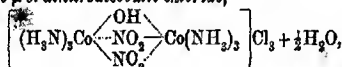
[With EMIL BINDSCHWILDER and F. WELTI].—*Dichlorohexammine- $\mu$ -nitro-ol-dicobalt-salts*,  $\text{YX}_2$ , where



The *chloride*,  $\text{YCl}_2$ , is obtained as a dark violet, crystalline compound when hexammine- $\mu$ -nitro-diol-dicobalt-chloride is heated on the water-bath with concentrated hydrochloric acid. It is sparingly soluble in cold water, and the violet solution in warm water changes to a red colour, from which the original hexammine- $\mu$ -nitrodiol chloride is precipitated by hydrochloric acid. The *nitrate*,  $\text{Y}(\text{NO}_3)_2$ , may be obtained from the chloride either by the action of concentrated nitric acid or sodium nitrate; dark violet crystals. With sodium sulphate, the *sulphate*,  $\text{Y}_2(\text{SO}_4)_3$ , is produced, and with sodium dithionate, violet crystals of the *dithionate*,  $\text{YS}_2\text{O}_6$ .

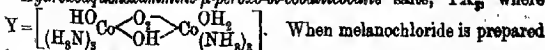
[With E. WELTI].—*Dibromohexammine- $\mu$ -nitro-ol-dicobalt-salts*,  $\text{YX}_2$ , where  $\text{Y} = \left[ (\text{H}_3\text{N})_3\text{Co} \begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{OH} \quad \text{NO}_2 \end{array} \text{Co} \begin{array}{c} \text{Br} \\ \diagdown \quad \diagup \\ \text{NO}_2 \quad \text{OH} \end{array} (\text{NH}_3)_3 \right]$  are obtained from the hexammine- $\mu$ -nitrodiol salts in a similar manner to the dichloro-salts. The *bromide*,  $\text{YBr}_2$ , is a greyish-black, crystalline powder, as also are the *nitrate*,  $\text{Y}(\text{NO}_3)_2$ , and the *dithionate*,  $\text{YS}_2\text{O}_6$ .

*Hexammine- $\mu$ -ol-dinitrodicobalt-chloride*,



is formed from dichlorohexammine- $\mu$ -nitro-ol-dicobalt-chloride by the action of nitrous acid in acetic acid solution. It is precipitated from solution in reddish-orange needles by the addition of nitric acid. Both the ol- and the nitro-linkings are very stable, since the salt can be recrystallised from hydrochloric acid.

*Hydroxoquinoxhexammine- $\mu$ -peroxo-ol-cobalticobalt salts*,  $\text{YX}_2$ , where



When melanochloride is prepared by the exposure of ammoniacal cobalt chloride solutions to the air at temperatures below  $5^\circ$ , and then worked up with silver nitrate, it yields a brownish-black nitrate in addition to the salts of the hexammine- $\mu$ -aminoperoxo-ol-cobalticobalt series. From this brownish-black nitrate, the pure *sulphate*,  $\text{Y}(\text{SO}_4)_2$ , may be obtained by a complicated process; shining brown crystals. On heating with concentrated sulphuric acid, it is decomposed with evolution of oxygen and nitrogen, the volumes of these gases obtained showing that the compound contains a peroxo-group and trivalent and quadrivalent cobalt. The

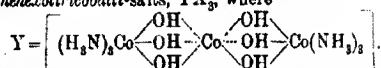
double salt with ammonium sulphate,  $Y(SO_4)_2 \cdot NH_4 \cdot H_2O$ , is precipitated when glacial acetic acid is added to a solution of the nitrate saturated with ammonium sulphate; black crystals. The following salts are prepared by double decomposition of the sulphate with various ammonium salts. The *chloride*,  $YCl_3$ , brown needles; *bromide*,  $YBr_3 \cdot H_2O$ , greenish-brown needles; *nitrate*,  $Y(NO_3)_3$ , blackish-brown leaflets. When a cold solution of the nitrate in water containing acetic acid is mixed with concentrated hydrochloric acid, small, greyish-black crystals of *trichlorohydroxo-hexammine-μ-peroxocobalticobalte chloride*,  $YCl_3$ ,

where  $Y = \left[ \begin{array}{c} Cl \\ HOCoO_2 \cdot Co \begin{array}{c} Cl_2 \\ (NH_3)_3 \end{array} \\ (H_2N)_3 \end{array} \right]$ , are obtained. The *nitrate*,

$YNO_3$ , is obtained from the chloride by precipitation with concentrated nitric acid. By the action of liquid ammonia on the chloride, hexammine- and chloropentammine-cobalti-chloride are obtained, proving that the two cobalt atoms of the original substance cannot be joined by a  $\mu$ -amino-linking, since such a linking is not severed by the action of ammonia.

When hydroxoquo-hexammine-μ-peroxo-ol-cobalticobalte sulphate is reduced with acetic acid and sodium iodide, and the liberated iodine destroyed with sodium thiosulphate, pale red crystals are obtained, which on treatment with ammonium bromide give bluish-red plates of hexammine-μ-acetato-diol-dicobalti-bromide, (q.v.). The arrangement of the ammonia molecules in the two series of salts is thus proved to be the same.

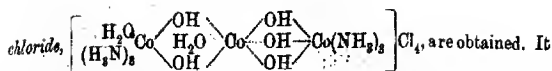
*Hexamminehexoltricobalti-salts*,  $YX_3$ , where



In the preparation of hexamminetriol-dicobalti-sulphate from chlorodiaquotriamminecobalti-sulphate (Abstr., 1908, ii, 43), a reddish-brown mother liquor is obtained, which, when strongly cooled, gives a green precipitate on the addition of concentrated hydrochloric acid. The green precipitate is dissolved in water, acidified with acetic acid, and precipitated as the impure sulphate by the addition of sodium sulphate. From the sulphate, by treatment with ammonium chloride, greenish-brown crystals of pure *hexamminehexoltricobalti-chloride*,  $YCl_3 \cdot 3H_2O$ , can be obtained. The *bromide*,  $YBr_3$ , is obtained from the chloride by the action of ammonium bromide, and the *dithionate*,  $Y_2(S_2O_8)_3 \cdot 2H_2O$ , by the action of sodium dithionate; brown crystals in both cases.

When these salts are decomposed by hydrochloric acid, the products are dichloroquo-triamminecobalt chloride,  $\left[ Cl_2Co \begin{array}{c} OH_2 \\ (NH_3)_3 \end{array} \right] Cl$ , cobaltous chloride, and chlorine. The formation of triammine salts shows that the six ammonia molecules are divided equally between two cobalt atoms, and the chlorine is a result of the reduction of the third cobalt atom from trivalent to bivalent cobalt. There are no  $\mu$ -amino-linkings, and hence the constitution given above.

When solutions of hexamminehexoltricobalti-salts are precipitated with concentrated hydrochloric acid in the cold, one of the ol-linkings is destroyed, and green crystals of *diaquo-hexamminepentoltricobalti-*



is not yet certain whether all the chlorine atoms are ionic in character.

For other complex metal ammonias, see Abstr., 1907, i, 482, 1012.

T. S. P.

**Tungstic Acid Hydrosol.** ALFRED LOTTERMOSER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1910, II, 70—71).—When a not too dilute solution of hydrochloric acid is added to a concentrated solution of sodium tungstate, a voluminous, gelatinous, white precipitate is formed. More dilute solutions remain clear at first, and afterwards slowly deposit the white precipitate in a more voluminous form. If the precipitate formed from very dilute solutions is repeatedly decanted with distilled water, a clear hydrosol may be obtained, which, however, is unstable, as it gradually becomes cloudy, and changes to a hydrosol which is yellow in reflected light. When more concentrated solutions are used, the voluminous, white precipitate gradually decreases in bulk, at the same time turning yellow; finally, the same yellow hydrosol is obtained as previously. If this yellow hydrosol is shaken, a silky lustre is noticeable in reflected light, although it appears clear in transmitted light; it is a suspension of relatively large particles, and gradually clears on keeping.

The above phenomena illustrate the gradual and continuous change from a solution, or molecular-disperse system, through a hydrosol, which is clear in both transmitted and reflected light, to a jelly. The jelly is not stable, however, and undergoes an irreversible transformation into a suspension.

T. S. P.

**Mutual Influence of Colloidal Tungstic and Molybdic Acids.** LOTHEAR WÖHLER and W. ENGELS (*Koll. Chem. Beihefte*, 1910, 1, 454—476).—Experiments are described which show that the precipitation which occurs when solutions of molybdates are acidified is due to the presence of tungstates. The readiness with which precipitation takes place is dependent on the proportion of tungstic acid present, and when this is present in very small amount, the temperature may be raised to nearly 100° before a precipitate is obtained. The precipitation is primarily due to the tungstic acid in the solution, and when this separates out, molybdic acid is simultaneously removed from the solution. Experiments have been made to determine the dependence of the composition of the precipitate on that of the solution. It is found that the quantitative extraction of tungstic acid in presence of large quantities of molybdic acid can be effected by precipitation with hydrogen sulphide in tartaric acid solution.

Dialysis experiments and ultramicroscopic observations indicate that molybdic acid can be obtained in colloidal form, and that colloidal molybdic acid is present in solutions of the molybdates. The precipitation which occurs on acidification of impure molybdate solutions is due to the mutual influence of the colloidal forms of tungstic and

molybdic acids. In consequence of this mutual influence, commercial tungstic acid always contains appreciable quantities of molybdic acid.  
H. M. D.

**Zirconium Sulphates. III.** The 4:8 Basic Zirconium Sulphate and its Hydrates. OTTO HAUSER and H. HERZFELD (*Zeitsch. anorg. Chem.*, 1910, 67, 369—375).—The salt  $4\text{ZrO}_2 \cdot 3\text{SO}_3$  containing water of crystallisation (Abstr., 1905, ii, 531), is so well defined as to be suitable for atomic weight determinations. Its properties have therefore been further studied. The ratio  $\text{ZrO}_2 : \text{SO}_3$  is very constant. When dried over dilute sulphuric acid, D 1.256, the salt contains  $15\text{H}_2\text{O}$ . It forms monoclinic, microscopic needles, D 2.50, and is very stable towards dilute acids. The loss of water when dried over sulphuric acid of increasing concentration is continuous until the hydrate  $4\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$  is reached, and the process of dehydration is not reversible. Careful heating for a long time at  $105-115^\circ$  yields a salt containing  $5\text{H}_2\text{O}$ , and the anhydrous salt, D 4.1, is obtained at  $300^\circ$ . The pentahydrate may be regarded as  $\text{Zr}_4(\text{SO}_3)_3(\text{OH})_{10}$ , and as the parent substance of the higher hydrates. An attempt to replace the hydroxyl by chlorine gave only indefinite products. C. H. D.

**Compounds of Thorium Chloride with Ammonia.** ÉDOUARD CHAUVENET (*Compt. rend.*, 1910, 151, 387—389).—The composition of the compounds prepared is given in tabular form, together with their heat of dissolution in hydrochloric acid, the approximate temperature of formation and decomposition, and in each case the heat of fixation of  $1\text{NH}_3$  on the preceding member of the series. The compounds mentioned are of the type  $\text{ThCl}_4 \cdot n\text{NH}_3$ , and may be classified into three groups: (1)  $n = 4, 6, 7, 12$ , and 18. These are obtained by treating thorium chloride with liquid ammonia, and allowing the product to remain at different temperatures. They are decomposed by water, and in a vacuum lose ammonia, forming the compound  $\text{ThCl}_4 \cdot 4\text{NH}_3$ . (2)  $n = 4, 6$ , or 7. The members of this group are prepared by leaving the chloride in contact with gaseous ammonia. They remain unaltered when placed in a vacuum or treated with water. (3)  $n = 6, 7, 12$ , or 18. These compounds are obtained by the addition of liquid ammonia to members of the second group; the first two terms of this group are identical with the last two of the second.

The compound  $\text{ThCl}_4 \cdot 4\text{NH}_3$  of the second group, is the only one in the whole series stable above  $120^\circ$ . At  $250-300^\circ$ , however, this loses hydrogen chloride and forms thorium tetramide, whilst at a red heat the amide  $\text{Th}(\text{NH}_2)_4$  is obtained.  
W. O. W.

**The Equilibrium Diagram of the Gold-Zinc Alloys.** G. G. URZOFF and RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1910, 67, 442—447. Compare Vogel, Abstr., 1909, ii, 896; Urzoff, this vol., ii, 43).—The differences between the results previously obtained by the two authors are discussed and explained. The existence of Urzoff's compound,  $\text{Au}_2\text{Mg}$ , is confirmed, as is that of Vogel's transformation to  $\text{AuMg}$ , and  $\text{AuMg}_2$ , on cooling to  $716^\circ$ . The curve representing the

change in concentration of the solid solution Au-AuMg on cooling has the form given it by Vogel; in the remaining curves Urazoff's data are to be preferred.

C. H. D.

## Mineralogical Chemistry.

**Ludwigite from Montana.** WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1910, [iv], 30, 146—150).—Ludwigite, a mineral hitherto known only from Morawitz, in Hungary, has been found at Philipsburg, Montana, as small spherulites, with a radiated structure and a dark green or nearly black colour, in metamorphosed limestone with large bodies of magnetite. Under the microscope the fibres give straight extinction and are strongly pleochroic (sea-green for vibrations parallel to their length, and chestnut-brown perpendicular to this). Embedded in the material is an olivine (perhaps forsterite), a carbonate (perhaps magnesite or chalybite), and a colourless fibrous mineral. The material analysed (anal. I) was, therefore, not quite pure; deducting forsterite, etc., the composition is as given under II, and neglecting water and alumina, the formula becomes  $4(\text{Fe,Mg})\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ .

	B <sub>2</sub> O <sub>3</sub>	MgO	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O (105°)	H <sub>2</sub> Q (>105°)	CO <sub>2</sub>	Total.
I. 13·48	39·04	5·79	23·73	8·35	1·31	0·97	0·90	0·36	100·93	
II. 16·94	33·78	7·27	37·37	—	2·27	1·24	1·13	—	100·00	
III.* [17·02]	23·83	15·34	35·67	—	—	0·51	0·82	0·90	100·00	

\* Also insoluble, 0·36.

A new analysis of the Hungarian ludwigite is given under III, agreeing with the formula previously given for the mineral, namely,  $3\text{MgO} \cdot \text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot \text{Br}_2\text{O}_3$ . The Montana ludwigite differs from this in having a portion of the ferrous oxide isomorphously replaced by magnesia.

L. J. S.

**The Play of Colour of Alexandrite.** OTTO HAUSER (*Zeitsch. angew. Chem.*, 1910, 23, 1464—1465).—Alexandrite, a variety of chrysoberyl, is dark green in daylight, but cherry-red in artificial light. This play of colour is independent of the crystallographic form of alexandrite, and is due to a slight admixture of chromic oxide, which is present partly in colloidal solid solution, and partly as an isomorphous mixture.

Solutions of chromium sulphate which have been gently boiled, of chromium thiocyanate, and alkaline chromite solutions show the same phenomenon, being green in daylight and red in artificial light. Such solutions contain chromium oxide partly in colloidal, and partly in molecular solution.

T. S. P.

**Effect of the Presence of Alkalis in Beryl on its Optical Characters.** WILLIAM E. FORD (*Amer. J. Sci.*, 1910, [iv], 30, 123—130).—The following analyses are of pink beryls from: (1) Mesa

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Grande, San Diego Co., California; (II) Pala, San Diego Co., California; (III) Madagascar:

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	CaO	FeO	K <sub>2</sub> O	Na <sub>2</sub> O	Li <sub>2</sub> O	Igni- tion.	Total.
I.	64.98	17.86	—	13.42	—	0.18	0.84	0.46	2.16	99.90
II.	n. d.	n. d.	—	n. d.	0.57	0.28	1.59	1.38	n. d.	—
III.	62.79	17.73	trace	11.43	1.70	—	1.60	1.68	2.65	99.58

The refractive indices of this material, and also of beryls rich in alkalis from Willimantic, Connecticut, and from Hebron, Maine, analysed by Penfield (1888) and by Wells (1892) respectively are:

Locality.	n.	n.	n - n.	Total alkalis.	Sp. gr.
Mesa Grande...	1.53157	n. d.	—	1.43	2.711
Willimantic ...	1.58455	1.57835	0.00620	1.15	2.73
Pala .....	1.59239	1.58488	0.00751	3.77	2.785
Madagascar ...	1.59500	1.58691	0.00809	4.98	2.79
Hebron .....	1.59824	1.59014	0.00810	6.33 †	2.80

\* Approximate. † Namely, CaO, 3.60; Na<sub>2</sub>O, 1.18; Li<sub>2</sub>O, 1.60.

It is thus seen that with a replacement of glucina by alkalis there is (with the increased molecular weight) an increase in the values of the refractive indices, birefringence, and specific gravity. L. J. S.

**Chemical and Optical Study of a Labradorite.** WILLIAM E. FORB and W. M. BRADLEY (*Amer. J. Sci.*, 1910, [iv], 80, 151—153).—Perfectly clear and almost colourless (the larger pieces showing a faint tinge of yellow), water-worn pebbles of labradorite from the Altai Mountains in Mexico (close to the New Mexico boundary) gave:

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Ignition.	Total.	Sp. gr.
51.24	30.84	13.59	3.76	0.17	0.73	0.24	100.57	2.718

This corresponds with albite : anorthite = 1 : 1.918. The iron is due to the enclosure of minute scales of hæmatite arranged parallel to the cleavages; these enclosures produce a metallic reflexion, as in the sunstone from Norway. The angle between the cleavages is  $cb = 85^{\circ}49'$ ; the cleavage  $b(010)$  is imperfect and difficult to obtain. The angles of optical extinction are: on  $b(010)$ ,  $-24^{\circ}37'$ ; on  $c(001)$ ,  $-12^{\circ}13'$ .

L. J. S.

**Axinite from California.** WALDEMAR T. SCHALLER (*Zeitsch. Kryst. Min.*, 1910, 48, 148—157).—Opaque, smoke-grey crystals of axinite, measuring up to 5 cm. across, are found loose in decomposed granite at Moosa Cañon, near Bonsall, in San Diego Co.; the associated minerals are quartz, epidote, and laumontite. Analysis I agrees with the formula:



Several analyses previously published are tabulated and found to agree closely with this formula, in which the atomic amount of calcium is constant, whilst the manganous oxide and ferrous oxide replace each other isomorphously. For the end members of the series, the names ferroaxinite,  $\text{Al}_2\text{BHCa}_2\text{FeSi}_2\text{O}_{18}$ , and manganaxinite,



are proposed. It is pointed out that the sp. gr. (3.268 to 3.358) of axinite increases progressively with the percentage of manganese.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	H <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	Total
I.	42.61	17.43	0.38	7.53	4.10	0.44	19.74	1.56	6.04	99.83
II.	42.79	16.38	—	4.22	8.76	0.09	19.21	1.85	[6.70]	100.00

Small, transparent crystals of axinite from the Consumes copper mine in Amador Co. are associated with epidote and quartz. Several new crystal-forms are noted. Analysis II, made on a small amount of not quite pure material, also agrees with the above formula.

L. J. S.

### Physiological Chemistry.

**Quantitative Investigations on the Absorption of Benzene from the Air by Men and Animals.** KARL B. LEHMANN, KARL GUNDELMANN, OTTMAR STÖHR, and R. KLEINER (*Arch. Hygiene*, 1910, 72, 307—326).—The benzene was inhaled mixed with air, and exhaled over cooled flasks containing liquid paraffin. The latter were afterwards warmed to 100° in a current of air, which was then lead through absorbers containing a mixture of nitric and sulphuric acids, and the benzene thereby converted into the dinitro-derivative, in which form it was weighed. In the human experiments, about 80% was absorbed. Experiments were also carried out with rabbits in various ways. In the majority, the tracheotomised animals breathed through a valve from a chamber in which benzene vapour was pressed in by means of air, and mixed with other air sucked into the chamber by a pump. It was also expired through cooled paraffin absorption flasks. The absorption in the first half-hours was about 37—54.5% of the benzene inspired. There is in most animals a fall in the percentage absorbed during this period, but the amount taken up during the next three or four hours remains constant in most cases. Individual animals showed, however, considerable variations, just as Nencki showed that there are considerable variations in the amount of benzene converted into phenol in different animals. These, perhaps, bear some relationship to the benzene absorbed from inspired air. S. B. S.

**Experiments Made on Mont Blanc, in 1909, on Variations in Glycæmia and Hæmatic Glycolysis at a Very High Altitude.** RAOUL BAYEUX (*Compt. rend.*, 1910, 151, 449—451).—The experiments were carried out on rabbits at Chamonix, and at an altitude of 4350 metres on Mont Blanc, under a pressure of 450 mm. In each animal blood was withdrawn from the heart, defibrinated, and the sugar estimated immediately in one part, and in the other after glycolysis had been allowed to proceed for an hour at 39°. The conclusions drawn are that the amount of sugar and the speed of glycolysis are both diminished at high altitudes, but that the variations are independent



of alterations in the animal temperature. Death supervenes when glycolysis is diminished to the extent of 60%. W. O. W.

**Origin and Importance of the Amyolytic Blood Ferment.** KURT MOECKEL and FRANZ ROST (*Zeitsch. physiol. Chem.*, 1910, 67, 433—485).—The amount of amylase in the blood of different species of animals varies considerably, and corresponds with the digestive power. The amounts present in the urine do not show great variations.

The amount of ferment in the blood may be increased by cold, and tends to increase under the influence of hunger. Animal diastase introduced per os, per rectum, and subcutaneously does not increase the blood diastase.

Pilocarpin causes an increase both of amylase and of maltase in the blood-serum. Phloridzin and adrenaline have no effect. Strychnine poisoning generally results in an increase of diastase in the blood.

Human diabetes is usually coincident with diminished amounts of diastase.

The diastase is partly eliminated in the urine, and a part becomes inactive in the body. Impermeability of the kidneys generally gives rise to a not very considerable increase of diastase in the body.

N. H. J. M.

**Question as to the Identity of Pepsin and Chymosin.** W. SAWITSCH (*Zeitsch. physiol. Chem.*, 1910, 68, 12—25. Compare Bang, Abstr., 1900, ii, 356; Hammarsten, *ibid.*, 1908, i, 588).—In Hammarsten's method for isolating pepsin from chymosin, the latter is not destroyed, but the properties of the ferment are so altered that samples usually show negative coagulating properties.

Calves' rennin when kept in a thermostat alters in properties and then resembles Bang's parachymosin.

Although ferment solutions from different kinds of animals have different properties, it does not follow that the pepsins of different animals are not identical. The differences in properties are mainly of degree of resistance or reactivity, and it is shown that a ferment solution from a single animal can also vary considerably in properties according to the conditions of the experiment, and the non-reactivity of the solution does not necessarily mean the absence of the ferment; it may be due to the conversion of the ferment into its inactive form. It is possible that the difference in behaviour of different solutions is due to the presence of compounds of pepsin with various substances.

J. J. S.

**Comparative Investigations on the Activities of Pepsin and Chymosin of Dogs and Calves.** OLAF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1910, 68, 119—159).—Infusions of dogs' and calves' stomachs have been examined, and it is shown that the peptic and coagulating effects are quite different. Both extracts were made to contain 0.2% hydrochloric acid. Although the infusion from dogs contained twice as much pepsin as that from calves, it was found that at dilutions 1/10—1/80 the dogs' extract was incapable of curdling cow's milk, whereas extracts of the same concentration from calves

readily produced coagulation. In the case of the canine extract, the curdling did not follow the ordinary time law. The difference in behaviour was not due to the fact that the extract from dogs contained inhibiting substances, as when added to calves' infusion it produced much the same effects as diluting the latter extract with 0.2% hydrochloric acid.

An increase in the acidity of the infusion had a more marked effect on the dogs' enzyme than on the calves, and, by the addition of acid, it was found possible to obtain solutions of the two infusions with equal curdling powers, but the peptonising powers of two such extracts were as 1:50 (calves:dogs).

Calcium chloride also had a greater accelerating influence than acid, and in this case also the effect was more marked in the case of the infusion from dogs' stomachs, but it was not found possible to prepare solutions of the two infusions identical as regards both peptonising and curdling properties.

The addition of either acid or calcium chloride to dogs' infusion restores the ordinary time law.

It is pointed out that the addition of calcium chloride to milk, as in Migay and Sawitsch's experiments (this vol., ii, 140), increases the acidity of the milk (compare Dam, Abstr., 1909, i, 278). The results obtained support the view that peptonising and coagulating effects are due to enzymes (dualistic view).

The view that the difference is entirely due to the fact that cow's milk contains substances which inhibit the action of dogs' enzyme does not appear tenable, as experiments have been made with casein solutions in place of milk, and in these experiments complete parallelism between the two effects could not be obtained. Arguments against the view that the infusions themselves contain substances with inhibiting properties are also brought forward.

J. J. S.

Utilisation in the Animal Organism of Protein Cleavage Products. EMIL ABDERHALDEN and PETER RONA (*Zeitsch. physiol. Chem.*, 1910, 67, 405—411. Compare Abderhalden and Prym, Abstr., 1907, ii, 897).—It is shown that the preparations employed in experiments with protein cleavage products contained practically only amino-acids. By the combined digestion of proteins, especially meat, with pepsin and hydrochloric acid, trypsin, and erepsin, complete hydrolysis is readily obtained in three or four weeks, and probably less.

N. H. J. M.

Digestion of Cellulose. II. The Ingestion of Cellulose by the Dog. HEINRICH VON HOESSLIN (*Zeitsch. Biol.*, 1910, 54, 395—398. Compare this vol., ii, 626).—The author criticises the technique of Lohrlich and Simon, and, quoting his own and Scheuvert's experiments, considers that there is no evidence of the absorption of pure white cabbage cellulose in the intestine of the dog.

G. S. W.

The Mechanism of the Influence of the Hardness of Water on Bodily Development. RAGNAR BERG (*Biochem. Zeitsch.*, 1910, 27, 204—222).—It has been shown previously that bodily develop-

ment is impeded by a want of calcium salts, and the same cause has a deleterious influence on the excretions and secretions,\* and that these factors bear accordingly a direct relationship to the hardness of water. The author has carried out experiments and collected statistics to find in what manner the hardness of water acts. He finds that there is no direct relationship between the mineral contents of vegetables and the hardness of water in the neighbourhoods in which they are grown. There is, however, a direct relationship between the contents of cooked vegetables and the hardness of water in which they are cooked, those vegetables which are cooked in hard water having a greater calcium content after cooking than those cooked in soft water. These results were derived from experiments both on natural water and water hardened by different calcium salts. The author also gives statistics showing generally that in neighbourhoods with hard water, the children are suckled by their mothers for longer periods than in neighbourhoods with soft water. The mineral contents of milk exerted no influence on the difference of digestibility of boiled and unboiled milk. The calcium salts of digested milk are soluble both in acid and alkaline liquids, and dialysable. The calcium that is rendered insoluble by rennet is apparently not present as inorganic salt.

S. B. S.

**The Inhibition by Potassium Cyanide of the Deleterious Action of Salt Solutions on the Fertilised Egg.** JACQUES LORS (*Biochem. Zeitsch.*, 1910, 27, 304—311).—It has been shown that if the fertilised egg of sea-urchins, placed in solutions of the chlorides of the alkali metals isotonic with sea-water, and be then returned to sea-water, they undergo cytolysis. It is now shown that this deleterious action can be inhibited if small quantities of potassium cyanide be added to the salt solutions. To explain the result, it is assumed that the hydrolytically dissociated part of the salt enters into action in the cell, the hydroxides of the alkali metals forming salts with the acid constituents of the cell, which undergo oxidation. The oxidation products act cytolytically, but are precipitated by the salts of dyad metals. Potassium cyanide acts by inhibiting this oxidation.

S. B. S.

**Action of Some Organic Salts of the Alkalis on Muscle, Blood Corpuscles, Protein, and Lecithin.** RUDOLF HÖBER (*Pflüger's Archiv*, 1910, 134, 311—336. Compare this vol., ii, 330, and Abstr., 1909, ii, 251).—Continuing his studies on the parallelism between the physiological and the physico-chemical properties of neutral salt solutions, the author has investigated the action of solutions of the alkali salts of a number of organic acids on the resting current in muscle, the diminution of muscular excitability, the coagulation of protein substances by heat, the precipitation of proteins, and the precipitation of lecithin. He finds that in all these actions the organic cations fall into approximately the same series, namely, tartrate, sulphate (formate, acetate, propionate, butyrate, valerate), chloride, iodide. The effects of those of which the names are enclosed in brackets are nearly equal. The sodium and lithium

salts of salicylic and benzoic acids exhibit, however, no such parallelism, and their actions are not reversible.

The hemolytic effect of the various salts is the same for blood corpuscles of different animals, and runs fairly parallel to their other actions already mentioned. The typical hemolytic substances, such as saponin and solanin, generate in muscle an irreversible resting current in the normal direction, and diminish to a corresponding degree its excitability.

R. V. S.

**Extractives of Muscles. XI. Nitrogenous Extractive Substances of Veal and Beef.** WLADISLAW SKWARZOFF (*Zeitsch. physiol. Chem.*, 1910, 68, 26—39. Compare Krimberg, Abstr., 1908, ii, 609).—Aqueous extracts of veal yielded carnosine (0.176), methylguanidine (0.022), and carnitine (0.019%).

N. H. J. M.

**Occurrence of Choline in Testicles of Oxen.** G. TOTANI (*Zeitsch. physiol. Chem.*, 1910, 68, 86—87).—The author finds that choline is a normal constituent of oxen testicles (compare Dixon, Abstr., 1901, ii, 259).

J. J. S.

**The Bile of Polar Animals. IV. The Bile of Seals.** OLAF HANSEN (*Zeitsch. physiol. Chem.*, 1910, 68, 109—118. Compare Abstr., 1909, ii, 819).—The bile of the following species has been examined: *Phoca barbata*, *P. groenlandica*, *P. foetida*, *Cystophora cristata*. In each case the bile contained much taurocholate and but little glycocholate, and hence the aqueous solutions were not precipitated by lead acetate, copper sulphate, alum, calcium chloride, or barium chloride. Ferric chloride gave precipitates containing appreciable amounts of colouring matter together with tannic acids. Most of the biles contained only small amounts of phosphatides. The numbers varied from traces in the case of *P. barbata* to 14% in the case of *Cystophora cristata*.

Bilirubin and urobilin could not be detected in the bile of *C. cristata*, and urobilin was absent from the gall of *P. groenlandica*, but was present in appreciable quantity in that of *P. barbata*.

A glycocholic acid, not identical with the ordinary acid, small amounts of  $\alpha$ -phocaetaurocholic acid, appreciable amounts of  $\beta$ -phocaetaurocholic acid, and an acid, probably taurocholic acid, were isolated from the bile of *P. barbata*. Of the bile acids present in *P. groenlandica*, 44.52% consisted of  $\alpha$ -phocaetaurocholic acid; appreciable amounts of the  $\beta$ -acid were also found.

Taurocholic acid and the  $\alpha$ - and  $\beta$ -phocaetaurocholic acids were also detected in the gall of *P. foetida*.

*Cystophora cristata* gave a glycocholic acid, probably glycocholic acid, small amounts of  $\alpha$ - and  $\beta$ -phocaetaurocholic acids, and much taurocholic acid.

J. J. S.

**The Neutral Sulphur of Urine and its Relationship to the Diazo-reaction and the Elimination of Proteic Acids.** MORITZ WEISS (*Biochem. Zeitsch.*, 1910, 27, 175—203).—The diazo-reaction of Ehrlich is according to more recent researches due to

the hydroxyproteic acids which contain sulphur. The author has accordingly investigated the quantitative relationship between the neutral sulphur and the diazo-reaction, and also the amount of hydroxyproteic acid excreted. He gives a summary of the results of other observers on the elimination of neutral sulphur, and also his own determinations. He concludes therefrom that the groups yielding neutral sulphur are derived partly from the ingested food and partly from the proteins of the organism (exogenous and endogenous portions). The latter yield larger quantities of neutral sulphur, and the latter is increased under conditions, such as the influence of toxic substances, which cause a break down of the body proteins. In tuberculosis of the lungs, the neutral sulphur excreted increases both absolutely and relatively, and there is also a corresponding increase in the Ehrlich diazo-reaction. In carcinoma, the largest quantities of neutral sulphur were found. It appears, therefore, as if the neutral sulphur may be regarded as a measure of the amount of hydroxyproteic acids excreted.

S. B. S.

**The Excretion of Ethereal Sulphates and Glycuronic Acids after Administration of Aromatic Compounds.** FELIX STERN (*Zeitsch. physiol. Chem.*, 1910, 68, 52—68).—Experiments have shown that after the administration of aromatic substances there is a considerable increase in the amounts of glycuronic acid excreted, even when the preformed sulphuric acid is not completely exhausted. The increase in the ethereal sulphates takes place more promptly than an increase in the glycuronic acid, especially when indole and cresol are used.

The amount of ethereal sulphates gives a sure measure for the excretion of aromatic compounds when only small amounts are present. With large quantities of aromatic substances, account must be taken of both ethereal sulphates and glycuronic acid (compare P. Mayer, *Abstr.*, 1902, ii, 520, 616).

J. J. S.

**Behaviour of Benzoic Acid in the Organism of Fowls in Presence of Glycine.** J. YOSHIKAWA (*Zeitsch. physiol. Chem.*, 1910, 68, 79—82).—The organism of fowls is not able to effect the synthesis of hippuric acid from benzoic acid and glycine fed simultaneously.

N. H. J. M.

**Behaviour of Phenylacetic Acid in Fowls.** G. TOTANI (*Zeitsch. physiol. Chem.*, 1910, 68, 75—78).—When consumed by fowls, phenylacetic acid combines with ornithine with the production of phenylaceto-ornithuric acid, which probably has the constitution  $\text{CH}_3\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot[\text{CH}_2]_4\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ .

N. H. J. M.

**Physiological Degradation of Acids and the Synthesis of an Amino-acid in Animals.** FRANZ KNOOP (*Zeitsch. physiol. Chem.*, 1910, 67, 489—502).— $\alpha$ -Amino-acids, after parting with the amino- and carboxyl groups, are broken down in a manner similar to the next lower fatty acids. They may be acetylated in the bodies of animals.

$\alpha$ -Ketonic acids may take up nitrogen in organic combination in the bodies of animals with production of optically active  $\alpha$ -amino-acids.  $\alpha$ -Hydroxy-acids may also be converted into  $\alpha$ -amino-acids.

N. H. J. M.

Physiological Actions of an Ergot Base and of  $\beta$ -Iminazolyl-ethylamine [ $\beta$ -Amino-4-ethylglyoxaline]. D. ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1910, 54, 387—394).—A physiological comparison is made of  $\beta$ -amino-4-ethylglyoxaline and a base from ergot which exerts a specific action on the cat's uterus. The conclusion is drawn that they are not identical (compare, however, Barger and Dale, this vol., ii, 736).

G. S. W.

Innurement to Adrenaline. LEO POLLAK (*Zeitsch. physiol. Chem.*, 1910, 68, 69—74).—Experiments with rabbits showed that injection of  $r$ -adrenaline during a prolonged preliminary period had as little protective action on the effect of  $l$ -adrenaline as the employment of  $l$ -adrenaline itself.

N. H. J. M.

Behaviour of Pyridine in the Organisms of Goats and Pigs. G. TOTANI and Z. HOSHUI (*Zeitsch. physiol. Chem.*, 1910, 68, 83—84).—Experiments in which two goats and a pig, fed on an exclusively vegetable diet, received different amounts of pyridine, injected subcutaneously, showed that methylpyridine is produced and is eliminated in the urine.

N. H. J. M.

[Physiological] Action of Cholin. FRANZ MÜLLER (*Pflüger's Archiv*, 1910, 134, 289—310. Compare Abderhalden and Müller, this vol., ii, 725).—The fall of blood-pressure produced by choline is partly due to its action on the heart and partly to dilatation of the blood vessels. Choline also produces vasoconstriction, however, and this alone is observed on transfusion of the vascular system subsequently to the action of atropine. Choline acts on intestinal muscle both when the plexus has been removed and when it has not. Experiments with isolated muscle from the intestine, uterus, and iris show a great analogy to the action of physostigmine. The occurrence of a rise of pressure after atropine plus choline is probably due to paralysis of the dilatatory elements of the walls of the vessels by the atropine.

R. V. S.

The Influence of Quinine on Experimental Trypanosome Infection. JULIUS MOROENROTH and L. HALBKSTÄDTER (*Sitzungsber. K. Akad. Berlin*, 1910, 732—748).—The prophylactic action of quinine and various quinine derivatives, such as cinchonine, equinine, hydrochloroquinine, and hydrochloroisquinine was investigated. Under certain conditions a marked prophylactic action could be ascertained, and was manifested by the longer duration of the life of mice after infection with trypanosome strains. After peritoneal injection, even when the dose of alkaloid was almost toxic to the animal, no protection was obtained. After subcutaneous injection, the protection was more marked, and it was more marked still when the drug was taken *per os*.

The authors discuss the theory of these results, and regard the total action of the drug on the host ("organoergy") as the product of two factors, "organotropy"  $\times$  sensitiveness.

In a similar way the action on the parasite ("parasitergy") is also a product of the factors, "parasitotropy"  $\times$  sensitiveness. When "organoergy" is greater than "parasitergy" the drug will injure the host without killing the parasite. In the reverse case, the drug can exert action on the parasite.

S. B. S.

**Negative Ferric Hydroxide. III. Arsenic and Iron.** HERMANN W. FISCHER and ERICH KUZNETZKY (*Biochem. Zeitsch.*, 1910, 27, 311—325. Compare this vol., ii, 856).—Numerous experiments on animals, carried out chiefly with rabbits, were undertaken with a view to determine the action of colloidal ferric hydroxide as an antidote to arsenic poisoning. The positive ferric hydroxide had a slight antidotal action, and the negative colloid a somewhat stronger action. The conclusion was drawn, however, that a satisfactory antidote in the form of a colloidal ferric hydroxide could not be obtained. S. B. S.

### Chemistry of Vegetable Physiology and Agriculture.

**Abiotic Action of Ultra-violet Rays of Chemical Origin.** EUGÈNE TASSILLY and R. CAMBIER (*Compt. rend.*, 1910, 151, 342—344).—The flame of carbon disulphide burning in nitric oxide is shown to have a feeble sterilising action on water containing bacteria exposed to its light. Such a flame shows bands in the region  $\lambda$  3400—4900 Ångström units, and it is to the rays of this part of the spectrum that the flame appears to owe its abiotic properties (compare Cernovodeanu and Henri, this vol., ii, 332). W. O. W.

**Theory of Disinfection.** REGINALD O. HERZOG and R. BETZEL (*Zeitsch. physiol. Chem.*, 1910, 67, 309—313).—Silver nitrate is taken up by yeast as in a process of adsorption, and chloroform behaves similarly. In the case of formaldehyde, a constant amount is fixed by the yeast independently of the concentration. Phenol is not taken up by yeast.

N. H. J. M.

**Bactericide Value of Thymol.** ERNST WILLY SCHMIDT (*Zeitsch. physiol. Chem.*, 1910, 67, 412—432).—The action of thymol is very uncertain, and its employment in digestion experiments, especially those of long duration, with alkaline reaction should be discontinued. When animal and vegetable proteins are subjected to the action of a tryptic ferment in presence of thymol, misleading results may be obtained, owing to the bacteria attacking both the ferment and the protein.

N. H. J. M.

**Action of Anodic and Cathodic Liquids on Germination**  
 HENRI MICHELEA (*Bull. Acad. roy. Belg.*, 1910, 391—403. Compare this vol., ii, 232).—It has been shown previously (*loc. cit.*) that if wheat is allowed to germinate in contact with a  $N/100$ -solution of potassium chloride, through which an electric current is passed, the grain in the "anodic liquor" (that is, in that part of the solution near the anode) germinates less freely than that in contact with the "cathodic liquor," and the same difference is observed if wheat is allowed to germinate separately in such liquors, the electrodes having been removed, whence it is concluded that the effect of such liquors on germination is not due to electric charges on the ions, but to changes induced in the liquors by the passage of the current. In the present investigation an attempt is made to ascertain the nature of these changes, and the reasons for their influence on the germination of wheat. The initial salt solutions were centinormal in all cases. Filtration of the liquors has little influence. With sodium chloride or nitrate, cathodic liquor is more favourable to germination than anodic liquor, a mixture of the two is intermediate, and an unelectrolysed solution is better than any of the other three. The same is true of potassium nitrate or chloride, except that in the former case the cathodic liquor is more favourable than the unelectrolysed solution as regards leaf formation. For mixtures of potassium and sodium chloride, the unelectrolysed solution is better than the cathodic liquor. Using Liege water, or water distilled in glass vessels, the cathodic liquor is more favourable than the anodic liquor, although for the distilled water the difference is slight.

It is unlikely that these results can be explained by Aso's work (this vol., ii, 439), although they may be accounted for by de Heen's suggestion, that the cathodic liquor contains ionic chains broken at negative points, since such chains may be more favourable to the germination of wheat than the ionic chains with positive ends, present in anodic liquors. Moulds (*Mucor*, spp.) always develop freely in the anodic liquors, whence it seems likely that the protoplasm of *Mucor* is different from that of the higher plants. T. A. H.

**Origin of Osmotic Effects. III. The Function of Hormones in Stimulating Enzymic Change in Relation to Narcosis and the Phenomena of Degenerative and Regenerative Change in Living Structures.** HENRY E. ARMSTRONG and E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1910, 82, B, 588—602. Compare *Ahstr.*, 1909, ii, 387; this vol., ii, 668; also Guignard, *Ahstr.*, 1909, ii, 823; Mirande, *Ahstr.*, 1909, ii, 824).—When a leaf of cherry-laurel is exposed to the vapour of an anæsthetic, hydrogen cyanide is liberated; this is easily detected by means of Guignard's sodium picrate paper, and affords a delicate indication of the occurrence of enzymic change in the leaf. Not only the common anæsthetics, but most organic vapours, act as excitants, for example, toluene, benzene, naphthalene, carbon disulphide, volatile alcohols, and esters of acids of the acetic series, etc. Ammonia is very active, and carbon dioxide, benzaldehyde, and hydrogen cyanide also promote the change. Weak solutions of mineral acids, alkalis, and most salts are inactive, but the simpler organic



acids, mercurio chloride, cadmium iodide, and sodium and potassium fluorides all pass into the leaf from solutions. The behaviour of the laurel leaf resembles very closely that of the barley grain (compare A. J. Brown, *Abstr.*, 1909, ii, 386). It is proposed to divide substances other than colloids into two sub-classes, according as they will or will not pass through differential septa, such as occur in the barley grain and the laurel leaf. The term "*hormone*," introduced by Starling, is applied to the former sub-class.

Experiments show that water actually passes into the leaf together with the hormone, and that not only is hydrogen cyanide liberated and water absorbed, but that the amount of reducing sugar in the leaf is greatly increased.

The hypothesis is advanced that when introduced into the living cell, substances generally which are not attractive to water exercise stimulative effects that are primarily mechanical, molecules of the hormone being interposed between the molecules in the cell by the change in the osmotic state and the activity of the medium raised, so that an influx of water from other regions takes place. Possibly the mere dilution thus effected is determinative of change; contact being established between hydrolyte and hydrolyst, degenerative changes are set up which tend to increase in intensity as the products of change (hydrogen cyanide and benzaldehyde) in turn exercise a similar stimulative influence; gradually enzymes are set free which can attack the various hydrolytes stored in the cell.

From this point of view, the phenomena of change in living structures, especially muscle and nerve, are considered, also the phenomena of narcosis, the regulation of respiration, and the physiological effect of alcohol and of drugs generally. The hypothesis also affords an explanation of a number of more recent observations on plant metabolism.

E. F. A.

**The Presence of Free Hydrogen Cyanide in Plants.** CIRO RAVENNA and MARIO TONEGUTTI (*Atti R. Accad. Lincei*, 1910, [7], 19, ii, 19—25).—Free hydrogen cyanide does not appear to be present in the leaves of the cherry-laurel, or occurs in them only in traces. This result is obtained when the leaves are immersed one by one in boiling water, so that the enzymes are destroyed instantaneously. When the destruction of the enzymes is less rapid, free hydrogen cyanide produced by their activity may be found, as, for instance, when a mass of leaves is placed in boiling water, the temperature of which is thereby reduced for a short time. That the acid may be formed in such a way is shown by the fact that mixtures of amygdalin and emulsin wrapped in paper yield it under these conditions. The leaves lose hydrogen cyanide to a much greater extent when dried slowly at the ordinary temperature than when the desiccation is carried out at 130° (compare Couperot, *Abstr.*, 1909, ii, 257), but no hydrogen cyanide is evolved during the process.

R. V. S.

**Action of Vapours on Green Plants.** MARCEL MIRANDE (*Compt. rend.*, 1910, 151, 481—483. Compare *Abstr.*, 1909, ii, 823; Mirande, *ibid.*, ii, 824; Heckel, *this vol.*, ii, 63).—A large number of

substances are mentioned as producing blackening in the leaves of the cherry-laurel when the plant is submitted to the action of the vapours. In some cases liberation of hydrogen cyanide also occurs, whilst in others this is set free without blackening taking place. The compounds employed in the experiments included hydrocarbons and their halogen derivatives, alcohols, phenols, acids, ethers, esters, aldehydes, ketones, amides, amines, and nitriles. W. O. W.

The Betaines Present in Plants and Stachydrine. R. ENGELANN (*Zeitsch. physiol. Chem.*, 1910, 67, 403—404).—Polemical (compare Schulze and Trter, this vol., ii, 743). The author claims priority in establishing the constitution of stachydrine, and also as regards the suggestion of the origin of betaines in vegetable tissues. J. J. S.

Synthetic Production of Asparagine in Plants. DMITRI PRIANT-SCHNIKOFF and J. SCHULOFF (*Ber. Deut. bot. Ges.*, 1910, 28, 253—264).—Pea seedlings supplied for thirteen days with ammonium chloride failed to produce asparagine, and the total nitrogen was not increased as compared with similar seedlings kept in water alone. Barley, on the other hand, showed a marked increase in total nitrogen, and produced a considerable amount of asparagine without reducing the amount of protein nitrogen.

When, however, calcium carbonate was added in addition to ammonium chloride, peas were able to take up nitrogen and to produce asparagine, and still better results were obtained when calcium sulphate was employed instead of carbonate. In the second experiment, the peas produced a small amount of asparagine from ammonium chloride alone, a result which is attributed to the somewhat higher temperature as compared with the earlier experiment.

If it should be shown that all the ammonia assimilated is converted into asparagine, it would follow that the latter is produced from malic (or fumaric) acid, and not from aspartic acid and ammonia.

N. H. J. M.

Enzyme Hydrolysing Aesculin and a Fat Splitting Enzyme in *Aesculus hippocastanum*. WILHELM SIGMUND (*Monatsh.*, 1910, 31, 657—670).—Aesculin is hydrolysed to dextrose and aesculetin by an enzyme, *aesculase*, present in the bark, seed coats, and cotyledons of the horse chestnut (*Aesculus hippocastanum*), but not in the buds or leaves. Aesculase is without action on amygdalin. The cotyledons also contain a fat-splitting enzyme hydrolysing olive oil. E. F. A.

Constituents of Asparagus. J. LOUIS WICHERS and BERNARD TOLLENS (*J. Landw.*, 1910, 58, 101—113).—The results of analyses of asparagus roots in April and July showed that both the main and the side roots contained considerably more sugar, and readily hydrolysed hemicellulose at the earlier than at the later period of growth. The main root contained more cellulose and furfuroids than the side roots and both contained more in July than in April. The percentage of

total nitrogen was considerably higher in the side roots than in the main roots, and increased from April to July in the former, remaining almost the same in the latter.

The main roots contained more ash and mere potash in April than the side roots, whilst in July the side roots contained more potash and about the same amount of total ash as the main roots. The amount of phosphoric acid was considerably higher in the side roots than in the main roots, especially in July.

The results indicate that the organic constituents of asparagus cut from April to July are derived from the reserve substances of the roots, especially the thin side roots.

N. H. J. M.

**Carbohydrates of Asparagus.** J. LOUIS WICHERS and BERNARD TOLLENS (*J. Landw.*, 1910, 58, 113—116).—The expressed juice of asparagus was found to contain only reducing sugars (dextrose, 0.89%; lævulose, 1.55%), and no polysaccharides. Mannitol is probably present.

The roots contain dextrose and lævulose, and probably sucrose. Galactose was not found.

N. H. J. M.

**Presence of Stachyose (Manneotetrose) and of a Glucoside Hydrolysed by Emulsin in the Roots of Eremostachys laciniata.** JOSEPH KHOURI (*J. Pharm. Chim.*, 1910, [vii], 2, 211—213).—In a previous paper (this vol., ii, 151), the presence of a glucoside hydrolysed by emulsin in the leaves and twigs of this plant was announced. It is now shown that the roots also contain a glucoside of this type, and, in addition, stachyose, which was isolated in a pure state by Piaux's method (*Abstr.*, 1909, ii, 338).

T. A. H.

**Chemistry of the Higher Fungi. V. Maize Blight (*Ustilago Maydis* Tulane).** JULIUS ZELLNER (*Monatsh.*, 1910, 31, 617—634. *Comparo Abstr.*, 1909, ii, 922).—The following substances were found to be present in ripe spores (collected in September) freed by sifting from the degenerated tissues: Ergosterol-like substances, oleic acid, solid and volatile fatty acids, lecithin, glycerol, resins (soluble and insoluble in light petroleum), sclerotic acid, phlobaphen, tannin, mannitol, erythritol, dextrose, trimethylamine, ustilagine, proteins, amanitin, an inverting ferment, a fat-decomposing ferment, an amorphous base, a carbohydrate soluble in alkali, and chitinous substances.

The spores contained 89.14% dry matter and 4.14% ash of the following composition:

K <sub>2</sub> O.	Na <sub>2</sub> O.	CaO.	MgO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Cl.	P <sub>2</sub> O <sub>5</sub> .	SO <sub>3</sub> .	SiO <sub>2</sub> .	C and loss.
52.02	0.40	1.74	3.90	1.04	4.33	17.46	4.49	4.14	6.63	

N. H. J. M.

**Chemistry of the Higher Fungi. VI. Relations of the Higher Parasitic Fungi and their Substrate.** JULIUS ZELLNER (*Monatsh.*, 1910, 31, 635—641).—The composition of the parasitic fungi depends, in the first place, on their systematic position,

and many of their chemical characteristics are shared by saprophytic fungi. Their composition is also influenced by the host plant; wood fungi contain diastases and maltase; maize blight an invertase, etc.

The fungi attack the host plant partly by means of ferments, which render soluble the insoluble constituents of the plant, and partly by the direct withdrawal of plant constituents. There is probably, in addition, secretion from the parasite, sometimes of harmless or even useful substances, and sometimes of toxic substances. N. H. J. M.

**Occurrence of Organic Basic Substances in Yellow Boletus.** K. YOSHIMURA (*Zeitsch. Nahr. Genussm.*, 1910, 20, 153—155).—The author has separated the following bases from a specimen of yellow boletus (*Boletus edulis*), 1 kilogram of the air-dried fungus being found to contain: adenine, 0.12 gram; histidine, 0.14 gram, and trimethylamine, 0.15 gram. Arginine and choline were not present. W. P. S.

**Occurrence of Gentiopiricin in Roots and Stems of Gentiana pneumonanthe.** ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1910, [vii], 2, 149—153).—Application of Bourquelot's methods of detecting glucosides and sugars in plants (Abstr., 1902, ii, 55; 1907, ii, 540) showed that the roots of this plant probably contained sucrose, gentianose, and possibly a third sugar, and indicated the presence of a glucoside, hydrolysed by emulsin. The glucoside was isolated by Tanret's method (Abstr., 1905, i, 655), and proved to be gentiopiricin (compare Abstr., 1910, ii, 234). The stems, bearing leaves and flowers, also contain sugar hydrolysed by invertase, and two glucosides hydrolysed by emulsin, one of which was isolated and proved to be gentiopiricin. T. A. H.

**The Hellebore Group. I.** OSCAR KELLER (*Arch. Pharm.*, 1910, 248, 463—467).—*Nigella damascena* and *N. aristata* are the only members of the *Nigella* group which contain appreciable quantities of alkaloids; the former contains only damascenine, whilst the latter contains this alkaloid and its methyl and dimethyl homologues. On the assumptions that formaldehyde is the first assimilation product and that it can function as a methylating agent in the plant, the presence of the methylated alkaloids in *N. aristata* may be due to the greater development, the denser foliage, and the larger area of the leaves, factors which would condition a greater assimilative power, and therefore a more copious production of the first assimilation products, in *N. aristata* than in *N. damascena*. This idea, that the external form of plants, the greater or smaller development of their leaves, influences the composition of the alkaloids, and probably also of other substances, in the plants, is to be tested by an examination of members of other families. Obviously as many species as possible of a family must be examined, and a knowledge of all the bases therein be obtained. The groups of the family Ranunculaceae have been selected, and are classified according as they are non-poisonous, poisonous but free from alkaloids, or contain alkaloids. At present the author is dealing with the groups *Helleborus*, *Aquilegia*, *Caltha*, and *Delphinium*; the

alkaloids in plants of the last group are of especial interest (see following abstract). C. S.

**The Hellebore Group. II. New Delphinium Bases.** OSCAR KELLER (*Arch. Pharm.*, 1910, 248, 468—475).—The seeds of *Delphinium staphysagria* have long been known to be poisonous and to contain an alkaloid. The author now finds that the seeds of *D. consolida* contain at least three alkaloids. The seeds are extracted four times for four to eight days with 95% alcohol containing 0.5% hydrogen chloride. The extracts are concentrated and water is added, the pasty precipitate is removed, and the filtrate, after being concentrated on the water-bath, is extracted with chloroform-ether, the extraction being repeated after the solution has been basified. The crude bases removed from the chloroform-ether extracts by 5% hydrochloric acid are isolated as the hydrochlorides, a solution of which, after being basified with ammonium hydroxide, is extracted with ether and with chloroform; the ethereal solution slowly deposits large, hexagonal prisms of a substance *A*. The ammoniacal filtrate is neutralised by hydrochloric acid, basified by sodium hydroxide, and again extracted with ether and with chloroform, whereby a further quantity of crystalline matter, apparently identical with *A*, is obtained. The amorphous substance recovered from the ether and the chloroform can be separated into two portions, one soluble, the other insoluble, in ether. These portions, which are probably mixtures, have not yet received further attention.

The substance *A* separates from alcohol in colourless, hexagonal plates, m. p. 195—197°, reacts strongly alkaline in solution, does not form crystalline salts, acts as a very powerful poison when injected into cold-blooded animals, and resembles, but certainly is not identical with, Merck's delphinine *pur. crystallisat.* The latter is shown, by crystallisation from alcohol and mechanical separation, to be a mixture of a substance, m. p. 187.5°, crystallising in hexagonal plates, and another substance, crystallising in tufts of short needles, which softens at 187° and darkens, but is not fused, at 250°. C. S.

**Chemical Examination of the Tuberous Root of Ipomoea horsfalliae.** FREDERICK B. POWER and HAROLD ROBERTSON (*Amer. J. Pharm.*, 1910, 82, 355—360. Compare Abstr., 1908, ii, 725; 1909, i, 819).—The root, dried in a water-oven and ground, yielded by extraction with hot alcohol 2.5% of a dark brown, spongy resin, having  $[\alpha]_D^{20}$  -28.4° in alcohol, after decolorisation by animal charcoal. On successive extraction with (1) light petroleum, (2) ether, and (3) alcohol, it furnished the following three fractions: (1) a soft brown resin, containing (a) a substance, m. p. 132—133°, giving the colour reactions of a phytosterol, and (b) a mixture of unsaturated oily acid, with a crystalline acid, m. p. 56—58°; (2) a soft brown resin containing (a) probably a dihydric alcohol of the ipuranol type (*loc. cit.*); (b) resins, soluble in sodium carbonate or hydroxide; (3) resin containing some glucosidic material.

The crude alcoholic extract referred to above yields on steam-distillation traces of formic and butyric acids, whilst that portion (not

resinous matter) soluble in water contained (a) traces of a fluorescent substance, probably  $\beta$ -methylascorbin, already shown to occur in jalap resin (Abstr., 1909, i, 819), and (b) a sugar yielding *d*-phenyl-glucosazone and indefinite extractive matter precipitated by lead acetate. The root also contained much starch. T. A. H.

The Occurrence of Hemicellulose in the Pods of *Pisum sativum* and *Phaseolus vulgaris*. ERNST SCHULZE and U. PFENNINGER (*Zeitsch. physiol. Chem.*, 1910, 68, 93—109).—The nitrogen-free extract of the pods both of *Pisum sativum* and of *Phaseolus vulgaris* is rich in hemicellulose, and the amount increases as maturation advances; thus the dried, unripe pods of *Pisum* contained 16—19% of hemicellulose, while in the ripe pods the amount was 48.6%. On hydrolysis, galactose and arabinose are obtained. Full details of the hydrolysis are given, but the hemicellulose was not actually isolated. E. J. R.

Glucoside of *Pyrola rotundifolia*. Mlle. A. FICHTENHOLZ (*J. Pharm. Chim.*, 1910, [vii], 2, 193—203. Compare Abstr., 1908, ii, 995, and this vol., ii, 742).—By the application of Bourquelot's biological method, it was ascertained that this plant contained sucrose and a glucoside hydrolysed by emulsin, which was probably arbutin. The latter was isolated in a crystalline condition and identified. The slight differences between this preparation and pure arbutin were probably due to the presence of traces of impurity (methylarbutin?). The plant also contains invertase and emulsin. The quantity of sucrose in the plant is about three times as great in January and February as in May, but the proportion of glucoside remains unchanged. The plant can be dried without material change in the quantity of glucoside and sucrose present. T. A. H.

Influence of Copper and Manganese Sulphates on the Growth of Barley. W. E. BRENCULEY (*Ann. Bot.*, 1910, 24, 571—583).—Water-culture experiments in which barley plants were grown in solutions containing copper and manganese sulphate respectively in addition to the usual nutrients.

In the case of copper sulphate, it was found that in solutions containing from 20 down to 4 mg. of the crystallised salt per litre growth was checked in nearly every case, whilst 0.2 mg. per litre was without effect. No stimulating action was observed.

The results obtained with manganese sulphate indicate that whilst not actually toxic, like copper sulphate, moderate amounts of the salt considerably retard growth. Smaller amounts (10 mg. of the crystallised salt per litre, and less) seem to have a stimulating action.

N. H. J. M.

Fluorine in Wines. A. KICKTON and W. BEHNCKE (*Zeitsch. Nahr. Genussm.*, 1910, 20, 193—208).—The authors have detected the presence of fluorine in many different kinds of wines; one hundred and thirty-nine samples, consisting of Spanish, Portuguese, Italian, Greek, Turkish, Cape (S. Africa), French, German, and other wines, were examined, and in most cases a positive reaction was obtained.

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Vandam's test (Abstr., 1908, ii, 63) was found to afford the most trustworthy means of detecting the presence of fluorine compounds; when more than 1 milligram of fluorine is present in the quantity of wine used in the test, the depth of the etching is not a measure of the amount of fluorine, but if the etching is only rendered visible when the glass is breathed on, it may be concluded that less than 1 milligram of fluorine is present per 100 c.c. of wine. One Portuguese wine and about one-half of the number of Spanish wines examined contained very appreciable quantities of fluorine compounds; estimated by Treadwell and Koch's method (Abstr., 1904, ii, 841), the amounts found, calculated as sodium fluoride, varied from 4.6 to 11.1 milligrams per 100 c.c. of wine. These figures, in spite of the fact that the method was found to give too low results, indicate that certain Portuguese and Spanish wines contain added fluorine compounds, or that the wines have become contaminated by being stored in casks which have been treated with fluorides and insufficiently washed (compare Abstr., 1908, ii, 318).

W. P. S.

**Occurrence of Arsenic in Soils, Plants, Fruits, and Animals.** WILLIAM P. HEADEN (*Proc. Colorado Sci. Soc.*, 1910, 9, 345—360).—Arsenic, in a form which is slightly soluble in water, is widely distributed in the virgin soils of Colorado, especially in those which are marly, the amount varying from 2.5 to 5.0 parts per million. The marl underlying the soil is rather richer in arsenic, the quantity present ranging from 4 to 15 parts per million.

Soils on which crops have been grown which have been sprayed with arsenic preparations contain from 10 to 28 times as much arsenic as the virgin soils. Alfalfa, oats, potatoes, apples, and pears grown on such soils contain arsenic, which element is also found in the flesh and kidneys of animals which have been fattened on such alfalfa. It is also found in the urine of persons who have partaken freely of the apples grown on sprayed trees.

T. S. P.

**Transformation of Calcium Cyanamide in Soil. III.** CELSIO ULPANI (*Gazzetta*, 1910, 40, i, 613—666. Compare Abstr., 1908, i, 859).—The views now advanced by Löhnis (compare Löhnis and Moll, Abstr., 1909, i, 92) are in substantial agreement with those put forward by the author, except that they suppose the first product of hydration to be ammonium cyanoate, which is then converted into carbamide, whilst the author considers that the latter is formed directly. It is further pointed out that the idea that this transformation is effected by bacteria in the soil has now been generally abandoned, except by Kappen. In the author's opinion, however, the results of the latter are vitiated by the fact that in his experiments the presence of certain compounds (amino-acids, aldehydes) was not excluded, and these substances yield compounds with cyanamide which no longer give the reactions of cyanamide. Continuing his work on the subject, the author confirms his previous statement that the transformation of cyanamide in contact with soil proceeds in two stages, the cyanamide being first converted into carbamide, which is then transformed into ammonium carbonate. It has been found possible to isolate the

carbamide, and to estimate the ammonia formed. From an examination of the rate at which cyanamide is transformed when solutions of it at various concentrations are kept in contact with soil at different temperatures, it follows that in the first stage no micro-organisms are involved, for the following reasons: (1) the conversion proceeds most rapidly when the substances are first brought together, and it afterwards gradually diminishes; (2) the amount converted, increases with the concentrations of the solutions taken, and also proceeds in the same way at concentrations incompatible with life; (3) the conversion also takes place in the presence of antiseptics and with sterilised materials, and proceeds with increased velocity at  $100^{\circ}$ ; (4) sterilised charcoal converts cyanamide solutions into carbamide in the same circumstances as soil, although it is uncertain whether the further transformation into ammonia can be effected in this way. When the colloidal properties of soil are destroyed by heat or by the action of acids or alkalis, it loses the property of converting cyanamide solutions into carbamide, but acquires it again when mixed with colloidal substances, such as precipitated silicic acid, aluminium hydroxide, ferric hydroxide, aluminium silicate, and the amorphous hydrated silicates (zeolites) found in soils. It is probable that the colloids act catalytically on account of the large surface they present. The transformation is the more rapid the greater the surface of contact between soil and solution becomes. The conversion of the cyanamide is accomplished in two stages: in the former an accumulation of the substance takes place in the bounding layer between liquid and solid (corresponding with the rapid absorption during the first fifteen minutes), whilst in the second stage the actual decomposition of the material in this layer occurs. The question of the possible intervention of micro-organisms in the conversion of the carbamide into ammonia remains undecided. The ammonia formed is absorbed by the soil, and its disappearance naturally accelerates the reaction. It has been further found that the presence of soil, not only affects the rate of conversion of calcium cyanamide, but also alters its character, for whereas a solution of cyanamide tends to polymerise into dicyanodiamide, the same solution under the same conditions when in contact with soil yields no dicyanodiamide, but is converted into carbamide.

R. V. S.

**Effect of Carbon Disulphide on Decomposition Processes in Soils.** RICHARD SCHERPE (*Bied. Zentr.*, 1910, 39, 509–522; from *Arb. k. biol. Anstalt Land-, Forstwirts.*, 1909, 7, 353).—Pot and field experiments on the effect of carbon disulphide applied to soil alone and to soil manured with leather meal, green manure, and lime respectively. The results showed an increase in readily soluble forms of nitrogen in the soil under the influence of carbon disulphide, but failed to show whether leather meal was more rapidly broken down. In the case of green manure (potato leaves), treatment with carbon disulphide had no appreciable effect for two and a-half months, after which the soil so-treated became distinctly darker in colour than the soil which had no carbon disulphide, and showed a strongly alkaline reaction.

On limed soil carbon disulphide had much less effect. This is



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attributed to the production of a double compound of calcium thio-carbonate and hydroxide, which in time would be converted into polysulphides and then into hydrogen sulphide or injurious organic sulphur compounds.

N. H. J. M.

## Analytical Chemistry.

**Explosion Indicator.** NICOLAS TECLU (*J. pr. Chem.*, 1910, [ii], 82, 237—240).—An apparatus is figured and described, whereby the existence of an explosive gaseous mixture can be detected at a distance. The tube through which the gas is drawn by a pump bifurcates. One limb of the bifurcation consists of a glass explosion vessel, 15 c.c. in volume, closed at each end by stopcocks and provided with the usual platinum explosion wires. Sealed into the side of the vessel is a tube, provided with a stopcock and communicating with the atmosphere. Resting against the open end of this tube is a pendulous iron disk. The gaseous mixture under examination is drawn through the apparatus, the stopcocks at each end of the explosion vessel are then closed, the spark is passed, and the stopcock of the side-tube opened, whereupon the pressure in the explosion vessel, provided that an explosion has occurred, drives the pendulous iron disk against an electromagnet, thereby completing a circuit and sounding an alarm-bell at any desired place.

C. S.

**Improved Mouth-Blowpipe.** L. S. BAOSTER (*Chem. News*, 1910, 102, 89—90).—The blow-pipe is provided with a sliding two-way tap so that the air supply may be directed either to the blowpipe itself or, through a length of flexible tubing, into the glass tubing which is being heated by the blowpipe.

W. P. S.

**Siphon for Use with Carboys.** EDG. RAYMOND (*Bull. Soc. chim. Belg.*, 1910, 24, 327—328).—The siphon described is intended for use with concentrated acids, etc., and in other cases where it is inconvenient to start the action of the siphon by aspiration. The upper portion is made horizontal, and a cup or funnel, fitted with a three-way tap, is provided on this horizontal part near the point where it joins the vertical tube forming the short arm of the siphon; a short stoppered side-tube is provided at the top of the long arm of the siphon, and the lower end of this arm is fitted with a tap. The short arm of the siphon is placed in the carboy to be emptied, and some of the liquid from the latter is run into the cup and allowed to fill the long arm, the three-way tap being turned so as to allow of this being done; the tap at the lower end of the long arm is closed meanwhile. The stopper is then inserted in the short side-tube, the three-way tap is turned so as to connect the two arms and cut off the cup, and the siphon commences to work when the lower tap is opened. Should

there be but little liquid in the carboy, it may be necessary to repeat this operation of filling the siphon before it will work satisfactorily.

W. P. S.

**Modified Burette for Standard Alkali Solutions.** PAUL RUDNICK (*J. Amer. Chem. Soc.*, 1910, 32, 971).—Glass-stoppered burettes are objectionable for use with alkali hydroxide on account of the tendency of the stopcock to stick, the rapid wear which causes the tap to leak or break, and other disadvantages. The use of a glass tip connected to the burette by means of rubber tubing carrying a spring-clip is liable to introduce error.

The author has therefore employed a burette with a silver stopcock, and this has been found quite satisfactory. After it had been used for 30% sodium hydroxide for several weeks, it was still in as good a condition as when first received.

E. G.

**Apparatus for Gas Volumetric Determinations.** W. MÜLLER (*Zeitsch. angew. Chem.*, 1910, 23, 1556).—A simple and convenient apparatus is described for measuring the volume of gas liberated during a reaction. The gas expels water from a receiver which is so arranged that the water level is readily adjusted when the reaction is at an end. The volume of gas liberated is determined from the volume or weight of water expelled from the apparatus.

T. S. P.

**New Laboratory Apparatus.** THEO. GRZESCHLE (*Chem. Zeit.*, 1910, 34, 949).—The gas-washing bottle constructed by Adämmmer, in which the gas current is forced through two sieve-like plates, and consequently gets into a fine spray, is recommended. A rapid filtering arrangement in connexion with the water-air pump is described. It consists of a funnel holder fitted with a side-tube and three interchangeable ground funnels; the holder is placed on any suitable flask fitted with a rubber cork. A condensed drop-catcher to prevent any liquid from passing into the absorption liquid is next described. It consists of a pipette-shaped glass, into the upper end of which is sealed a horn-shaped tube. Just opposite the end of this tube the wall of the bulb is pressed inwards, and this causes the drop to flow down the side of the pipette.

L. DE K.

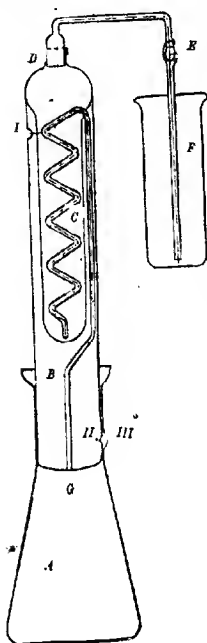
**A Convenient Condenser.** ARNOLD HAHN (*Chem. Zeit.*, 1910, 34, 809).—The apparatus is intended for the distillation of small quantities of liquids. The outer tube, resembling an ordinary condenser, is enlarged at the upper end to a bulb. The inner tube consists of the lateral tube of the distilling flask. The condenser, which is filled through the large opening in the bulb, is large enough to hold an amount of water sufficient to keep it cool during a distillation lasting for about half an hour, and if necessary iced water may be used. By means of a rubber tube with a clamp, the water may then be drawn off at the lower end.

L. DE K.

**Apparatus for the Estimation of Sulphur [in Iron, etc.]** GEORG PREUSS (*Chem. Zeit.*, 1910, 34, 840).—In the accompanying

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illustration, *A* is the flask used for the introduction of the sample and the acid, and *B* is the condenser attached to the flask by means of a ground joint. In the upper part of *B* is found a 5 mm. circular



opening, *I*, and a similar one at the lower end near *II*. Above the opening *II* in the flask *A* is found a rabbet, *III*. In the condenser *B* is placed a vessel *C*, which is half filled with water, which serves to absorb hydrochloric acid fumes, and *D* is a ground, hollow glass stopper which ends in a bent tube. Inside is placed a ground recoil valve *E*, which leads to the absorption vessel *F* containing cadmium solution. The tube *G* attached to the flask *A* conducts the gases through *B*, penetrates into the condensing vessel *C*, and, assuming a serpentine form, leads nearly to the bottom of the vessel; the hydrochloric acid fumes are thus completely condensed before reaching *F*. The recoil valve *E* prevents any regurgitation of the liquid in the absorption vessel *F*. *B* is filled with cold water, containing 50 grams of sodium hydrogen carbonate per litre, through the opening *I* by means of a wash-bottle.

After the operation is finished, the cooling water is emptied into the flask *A* by turning the condenser with opening *II* on to the rabbet *III* of the flask. The carbon dioxide evolved removes the last traces of hydrogen sulphide from the flask into the absorption liquid.

L. DE K.

**Estimation of Total Sulphur in Organic Matter.** HERMAN SCHREIBER (*J. Amer. Chem. Soc.*, 1910, 32, 977—985).—The peroxide method of estimating sulphur in organic substances is not altogether satisfactory for the following reasons. The amount of peroxide added varies with the material analysed and the rate at which it is added. The amount of acid added after fusion also varies in each case, and the solution must therefore be made alkaline again and re-acidified. Moreover, the fusions are liable to burn and blow out of the crucible. In view of these objections, the following method has been devised.

One gram of the material to be analysed is placed in a 100 c.c. nickel crucible, and 10 c.c. of a solution, containing 100 grams of sodium nitrate and 150 grams of sodium hydroxide in 500 c.c., are added. Five grams of crystalline magnesium nitrate are introduced and stirred with a platinum rod. The stirring rod and the sides of the crucible are washed down with the smallest possible quantity of water, and the crucible is then heated at 130° for an hour, and afterwards at 150—160°;

until the contents are dry. After the cover has been put on tightly, the temperature is raised gradually to  $180^{\circ}$  and the crucible is heated for thirty-five minutes at  $180-200^{\circ}$ , and afterwards with the Bunsen burner for half an hour. When the fused mass has solidified, the crucible is placed in a 600 c.c. beaker with 150 c.c. of water. Hydrochloric acid (13 c.c. of D 1.19) is now added, and the crucible is washed out with water. The beaker is heated for half an hour, and left in the cold during the night. The liquid is then filtered, and the residue washed. The filtrate is heated, and precipitated with 10% barium chloride solution.

The results obtained in a series of analyses of various materials by this method are compared with those obtained by the peroxide method. This comparison shows that the former method gives results about 0.1% lower than the latter, or about 0.064% lower than would be obtained by the absolute method. Both these discrepancies are well within the limits of experimental error.

In order to determine the effect of the salts in solution on the precipitation of the sulphate, comparative experiments were made by the new method and the peroxide method, in which definite volumes of dilute sulphuric acid were added to the solutions, blank experiments being carried out simultaneously. It was found that the new method gives results 0.1% too high when 3.5% of sulphur is present, and 0.3% too high when 8% of sulphur is present.

E. G.

**Gravimetric Estimation of Sulphuric Acid in the Presence of Alkali Metals.** YOGORO KATO and ICHISABURO NODA (*Mem. Coll. Sci. Eng. Kyōtō*, 1909—1910, 2, 217—228).—The concentration of a semi-normal solution of sulphuric acid was determined gravimetrically both in the absence of, and in the presence of, equivalent solutions of the chlorides of potassium, sodium, and ammonium. Determinations were also made with varying concentrations of the haloid salts, and with more dilute solutions of sulphuric acid.

Potassium chloride caused the greatest error in the determination. The ratio ( $R$ ) of salt to acid and the percentage difference ( $D$ ) between the results obtained in the absence of, and in the presence of, potassium chloride are connected by the equation:  $\log D = n \log R + K$ , where  $K$  is a constant. This is similar to the ordinary adsorption formula, so that it is probable that potassium sulphate is adsorbed during the precipitation of the barium sulphate.

Adsorption is diminished, but not completely, by diluting the solution. No adsorption takes place in the presence of magnesium chloride.

T. S. P.

**Apparatus for the Estimation of Arsenic.** ORIS D. SWERT (*J. Amer. Chem. Soc.*, 1910, 32, 962—965).—A new form of apparatus suitable for the estimation of arsenic by the Marsh-Berzelius, Gutzeit, and similar methods is described with the aid of a diagram. The chief advantages claimed for it are that it consists of fewer parts than most of the existing forms, and, whilst giving trustworthy results, is compact and portable.

E. G.

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**Precipitation of Arsenic Acid by Ammonium Molybdate.** G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 15—19).—The author has investigated the conditions requisite for the quantitative precipitation of arsenic acid by ammonium molybdate in neutral and acid solutions of different strengths. When precipitation is effected in solutions containing mineral acid, and having an acidity greater than 0.030% of hydrogen ions, the precipitate is yellow. Ammonium nitrate must be present, and the requisite quantity of ammonium molybdate depends on the concentration of the solution and its degree of acidity.

Precipitation is complete under the following conditions: 10 c.c. of a solution containing 0.080 gram of arsenic oxide are treated with 15 c.c. of a solution of ammonium nitrate containing 370 grams per litre, then with 60 c.c. of water and 2.5 c.c. of concentrated nitric acid (D 1.30); the liquid is boiled, and 1.60 grams of solid ammonium molybdate are added, the boiling being continued for three minutes. The precipitate is washed by decantation with a solution containing 50 grams of ammonium nitrate and 40 c.c. of nitric acid per litre.

In the case of neutral solutions and of solutions containing mineral acids, but having a smaller acidity than that given above, similar conditions are recommended. The precipitate obtained is white, and the washing is effected with a solution of ammonium nitrate, in which it is practically insoluble.

In the presence of organic acids (tartaric, oxalic, citric, succinic, and phthalic acids were employed) the white modification is usually precipitated. A large excess of ammonium molybdate is necessary.

Analysis of the yellow precipitate gave the value 1:24.34 for the ratio  $\text{As}_2\text{O}_5:\text{MoO}_3$  in it, whilst for the white modification the ratio was found to be 1:16.10. R. V. S.

**Detection of Arsenic Acid in Presence of Phosphoric Acid.** G. MADERNA (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 68—69).—The solution of the alkali salts of the two acids, rendered faintly acid with acetic acid and reduced to a small volume, is treated with 10—15 c.c. of a concentrated solution of ammonium nitrate, and when the mixture has been raised to boiling point about 1 gram of solid ammonium molybdate is added. When this has dissolved, the liquid is boiled for about one and a-half minutes. If arsenic acid is present, a white precipitate is formed. By this method 0.002 gram of arsenic acid can be detected in the presence of a large quantity of phosphoric acid. Salts of calcium, strontium, and magnesium do not invalidate the test, but render it rather less delicate. R. V. S.

**Rapid Estimation of Carbon in Steel and Other Iron Alloys.** R. AMBERG (*Chem. Zeit.*, 1910, 34, 904).—Johnson's process, which consists in burning the alloy in a current of oxygen, as a rule with the addition of any oxidising substance, and using a quartz combustion tube, is recommended (compare Abstr., 1906, ii, 630; 1908, ii, 630).

L. DE F.

**Apparatus for the Determination of Equivalents of Metals and for the Estimation of Carbon Dioxide both Directly and indirectly.** MANINDRA NATH BANERJEE (*Chem. News*, 1910, 102, 1-92).—The apparatus consists of a small flask fitted with a cork, through which pass the stem of a small tapered funnel, a short bent tube, and a delivery tube. The portion of the latter below the cork is provided with three bulbs, and the lower end is bent upwards so as to be level with the uppermost bulb. Concentrated sulphuric acid is filled to these bulbs, and serves to dry the gases liberated from the substance contained in the flask by the action of a reagent (sulphuric acid, &c.) introduced from the tapered funnel. The gases evolved may be collected in a suitable absorption tube and weighed, or their quantity determined by weighing the apparatus before and after the operation. Small hand-bellows and a drying tube are provided for passing a current of air through the apparatus to remove residual traces of gases.

W. P. S.

**Analysis of Amblygonite.** H. CORMINGEUF (*Ann. Chim. anal.*, 10, 15, 295-298).—The following method is recommended for the analysis of amblygonite, which is, essentially, lithium sodium fluorophosphate. Two grams of the finely divided sample are mixed in a platinum crucible with 4 grams of calcium oxide, and then heated over a blast-lamp for about fifteen minutes. When cold, the semi-fused mass is dissolved in dilute nitric acid, and the solution is evaporated to dryness. The silica is collected on a filter, and the phosphoric acid estimated in the filtrate by the bismuth method. After removing excess of bismuth (as sulphide) in the filtrate from the bismuth phosphate precipitate, the aluminium is precipitated in the usual manner. The filtrate from the aluminium hydroxide is treated with ammonium oxalate to remove calcium salts, and the sodium and lithium remaining in the solution are weighed together as their sulphates. The fluorine is finally separated from the sulphate mixture as its phosphate. Fluorine is estimated by difference.

W. P. S.

**Separation of Calcium and Magnesium.** ERNST MÜRMANN (*Monatsh. Chem.*, 1910, 49, 688-698).—Calcium may be separated with sufficient accuracy from magnesium by the oxalate process in its various modifications, either in ammoniacal or acetic acid solutions. However, as in the case of magnesite, the magnesium largely remains, the results are quite erroneous.

Attempts to remove the magnesium by means of barium hydroxide or to estimate the calcium in the filtrate, after precipitating the magnesium with sulphuric acid, proved quite unsuccessful even when using extremely dilute solutions.

The only successful way of obtaining a complete separation is to dissolve a solution of the mixed chlorides in 90% alcohol. The amount of alcohol should be approximately known, and a sufficiency of dilute sulphuric acid be added to secure its conversion into sulphate. The solution is then freed from any co-precipitated magnesium sulphate by repeated washing with the same alcohol.

L. DE K.

# ABSTRACTS OF CHEMICAL PAPERS.

**Estimation of Barium.** MAURICE HUYBRECHTS (*Bull. Soc. ch. Belg.*, 1910, 24, 281—283. Compare this vol., ii, 544).—Results of experiments are given which appear to indicate that the estimation of barium as sulphate is most trustworthy when the solution from which the precipitation is made contains about 0.5% of free hydrochloric acid; it is also advisable to use a considerable excess of the precipitant (10% ammonium sulphate solution). W. P. S.

**Estimation of Small Quantities of Lead in Alloys of Antimony, Copper, and Tin.** WOLFGANG MANN (*Chem. Zeit.*, 1910, 34, 917).—Ten grams of the alloy are dissolved in 45 c.c. of hydrochloric acid, D 1.19, and 5 c.c. of nitric acid, D 1.4, 10 grams of tartaric acid are added, and the whole is diluted to 300 c.c. When 10 c.c. of ammonia, D 0.91, is added until the liquid is about neutral, when another 100 c.c. of ammonia are added. Enough potassium cyanide solution is added until the liquid is colourless, and another extra 5 grams of sodium cyanide are introduced. After heating to 70°, a rapid current of hydrogen sulphide is passed. The impure lead sulphide is collected and washed with a hot solution of ammonium sulphide and potassium cyanide (50 grams of commercial ammonium sulphide and 10 grams of potassium cyanide in a litre of water; the liquid is heated until colourless). The sulphide is then dissolved in hydrochloric acid containing bromine, the bromine is boiled off, and, when cold, excess of ammonia is added, and also 5 grams of potassium cyanide. The lead is re-precipitated as sulphide, which is then redissolved in hydrochloric acid and bromine, and converted into sulphate by evaporating with addition of 10 c.c. of 50% sulphuric acid.

After weighing the lead sulphate as usual, it should be boiled repeatedly with ammonium acetate, and any insoluble residue allowed for. L. DE K.

**New Reaction for Copper.** RUDOLF UHLENHUTH (*Chem. Zeit.*, 1910, 34, 887).—The reagent is prepared by dissolving 0.5 gram of 1:2-diaminoanthraquinone-3-sulphonic acid in 500 c.c. of water with addition of 40 c.c. of aqueous sodium hydroxide, D 1.4. On adding the reagent to a solution of a copper salt so dilute that the usual test fails to detect it, there will still appear a blue coloration. The test seems to be conclusive for copper. L. DE K.

**Electro-deposition of Metals.** F. MOLLWO PERKIN and WILLIAM E. HUGHES (*Trans. Faraday Soc.*, 1910, 6, 14—18. Compare *SAR. Trans.*, 1907, 373).—The authors describe the various forms of rotating anode and cathode which they have tried for rapid electro-deposition of metals. In the most satisfactory apparatus, the anode is a closely wound spiral of iridium-platinum wire, rotating at 750—950 revolutions per minute within a fixed cathode, consisting of a cylinder of fine platinum gauze. The whole is placed in a tap funnel with a side tube in which a capillary electrometer can be dipped when potential measurements are desired. With this apparatus, 0.03735 gram of cobalt or 0.1265 gram of copper can be satisfactorily deposited in ten minutes. In making potential measurements, the apparatus described

land is used in conjunction with a potentiometer and mirror goniometer, a 10*N*-solution of ammonium nitrate being used as supporting solution. In depositing cobalt, the potential break occurs at 2 volt, with copper at 0.55 volt. With very low potentials, cobalt may be deposited on the anode.

R. J. C.

**Estimation of Copper as Anhydrous Cupric Sulphate.** ALBERT URA (*Bull. Soc. chim.*, 1910, [iv], 7, 832—834).—Although the traces of water are only removed with great difficulty from copper sulfate at 180—200° when the latter is a residue from a neutral sulfate solution, it is found that such a residue from a solution containing a little sulphuric acid can be freed easily from water and excess of acid at this temperature. It is suggested that by taking advantage of this fact, all copper compounds which can be readily converted into cupric sulphate, directly or indirectly, may be estimated as anhydrous cupric sulphate.

T. A. H.

**The Separation of Copper from Cadmium and Zinc by means of "Cupferron."** JOSEF HANUS and ARN. SOUKUP (*Zeitsch. Chem.*, 1910, 68, 52—56).—The results obtained agree with those of Biltz and Hödtke (this vol., ii, 550). The separation of copper from cadmium and zinc by means of this reagent has no advantage over the older methods.

C. H. D.

**Colorimetric Estimation of Manganese in Presence of Iron.** M. R. SCHMIDT (*J. Amer. Chem. Soc.*, 1910, 32, 965—967).—An account is given of the best mode of carrying out Walter's colorimetric method for estimating small quantities of manganese in presence of iron (*Chemical News*, 1901, 84, 239) so as to obtain accurate results with as great rapidity as possible. The method has been found suitable for estimating manganese in certain pharmaceutical preparations. It has been employed by Hillebrand in the analysis of minerals, and should also prove useful for the estimation of manganese in waters.

E. G.

**The Part taken by Atmospheric Oxygen in the Oxidation of Oxalic Acid by the Higher Oxides of Manganese.** K. PRODER (*Zeitsch. öffentl. Chem.*, 1910, 16, 270—283, 290—305).—When the available oxygen in pyrolusite is estimated by Lunge's method, the results are high if the hot solution is allowed to remain before titrating back. Air alone is without action on oxalic acid, the presence of a manganese salt being necessary. The oxidation is still further accelerated if titanium is present as well as manganese. By excluding air, or by using a concentrated solution of oxalic acid and titrating rapidly, results may be obtained which agree with those given by titration with ferrous sulphate.

In titrating oxalic acid with potassium permanganate, a small error arises from induced atmospheric oxidation if the titration is slow (five to ten minutes) and the solution is only slightly acid. This error is increased by the presence of manganese sulphate, and still more by titanium dioxide. Such additions give rise to error, even in strongly acid solutions titrated rapidly.



The formation of hydrogen peroxide, observed by Georgievsky (Springer (Abstr., 1900, ii, 631) and by Skrabal (Abstr., 1905, ii, 18), also occurs when oxalic acid acts on manganese dioxide, depends on the action of atmospheric oxygen, as it is not observed in the absence of air. When the titration of oxalic acid with permanganate is rapid, there is a compensation of errors, as the results are not low even when a stream of oxygen is passed through the apparatus. This must be attributed to the formation of hydrogen peroxide. The peroxide is only very slowly decomposed, even on boiling, by oxalic acid, except in the presence of titanium or of cerium.

For practical purposes, the error of the titration is negligible, even in contact with air, if the temperature is not above 50°, and the solution contains as much as 30 c.c. of sulphuric acid (1:1) to 200 c.c. of water, and the titration is performed rapidly. It is therefore possible to determine the approximate quantity of permanganate required by a preliminary titration, and then to warm the solution to 50° and to add the greater part of the permanganate at once. The addition of a manganese salt is undesirable.

The author also reviews the theory of the induced reaction.

C. H. D.

**Sulphurous Acid as an Etching Reagent for Metallographic Purposes.** SIEGFRIED HILPERT and EDWARD COLVER GLAY (*Zeitsch. anorg. Chem.*, 1910, 68, 63—68).—A dilute solution of sulphurous acid (1:25) reacts with iron, coating the surface with a thin layer of sulphide. This reaction may be used to develop the structure of cast iron and steel. Cementite is not attacked. Results obtained on etching austenite, martensite, and troostite differ somewhat from those given by other reagents, and the method is proved useful in distinguishing these constituents.

C. II. I.

**Precipitation of the Iron Group and the Composition of Certain Ferric Formates.** OLIN F. TOWER (*J. Amer. Chem. Soc.*, 1910, 32, 953—957).—The precipitation of iron, aluminium, and chromium as basic acetates is not very satisfactory, on account of the difficulty of filtering and washing the precipitate. Schulze (*Chem. Centr.*, 1861, 3) therefore recommended the use of ammonium formate for precipitating iron and aluminium, and this method has been studied by the author.

It has been found that both iron and aluminium can be completely precipitated by boiling with ammonium formate if the solution is sufficiently dilute. Filtration takes place more rapidly than in the case of the basic acetates. Chromium is not precipitated unless iron is present. The presence of ammonium chloride is desirable, as it causes the precipitate to form larger flakes, and thus facilitates filtration. The method of procedure which has been found to give the best results is described in detail.

Ludwig (*Arch. Pharm.*, 1861, [ii], 107, 1) and Schenrer-Kestn (*Compt. rend.*, 1863, 56, 1092) have stated that ferric triformate can be prepared by the action of formic acid on moist ferric hydroxide.

now found, however, that the product thus obtained has the composition  $\text{Fe}_2(\text{OH})_2(\text{CHO}_2)_2$ . The basic formate precipitated under usual conditions is represented by the formula  $\text{Fe}_3\text{O}_3(\text{OH})_2 \cdot \text{CHO}_2$ .  
E. G.

**Logalol Dimethyl Ether, a Delicate Reagent for Chromic Ferric Salts, and Nitrites.** JULIUS MEYERFELD (*Chem. Zeit.*, 34, 948).—If a 2% aqueous solution of the reagent is added to a solution of potassium dichromate acidified with sulphuric acid, a pinkish-red or, in very weak solutions, a yellow coloration is produced. Chloroform extracts the colouring matter and turns yellow. The test exceeds in delicacy the hydrogen peroxide test.

As a test for iron it is about equal to the thiocyanate test, and in the case of nitrites it is about as delicate as the reaction with potassium iodide and starch. The test is also obtained with potassium permanganate so diluted as to be colourless. It is essential that the reagent should be freshly prepared.  
L. DE K.

**Simple and Accurate Method for the Estimation of Titanium.** O. L. BARNEBY and R. M. ISHAM (*J. Amer. Chem. Soc.*, 32, 957—962).—The methods of estimating titanium, depending on the precipitation of titanioacid from solutions containing sulphurous sulphuric acids, and the volumetric method involving reduction of iron and subsequent titration with potassium permanganate, give unsatisfactory results. The methods in which the iron is reduced with sulphur dioxide or hydrogen sulphide, and the titanium precipitated with ammonia or by boiling with sodium or ammonium acetate and acetic acid, give high results when a large excess of iron is present. A new method is now described which gives accurate results, and has been found useful for the analysis of rutile and iron ores. The iron is removed by means of hydrofluoric acid in presence of sulphuric acid. The residue is evaporated to dryness and fused with sodium carbonate and a little sodium nitrate in order to convert the iron and titanium into insoluble ferric oxide and sodium titanate, and afterwards extracted with hot water to remove the soluble phosphates, silicates, and aluminates. The ferric oxide and sodium titanate are dissolved in hydrochloric acid, and the ferric chloride is extracted by means of ether. The remaining traces of iron are reduced with stannous dioxide and the titanous acid is precipitated by boiling with calcium hydroxide, and afterwards collected and converted into titanium oxide by ignition.

If the titanium is present only in small quantity, it can be estimated volumetrically. The solution, after extraction with ether, is heated on a water-bath and the ether is removed. When cold it is transferred to a Nessler's flask and treated with hydrogen peroxide, diluted to a particular volume, and compared with standard solutions of titanous acid in hydrochloric acid which have been similarly treated with hydrogen peroxide.

W. von E. Rosenheim and Schütte (*Abstr.*, 1901, ii, 244) have described a brownish-white compound obtained by the action of an ethereal solution of hydrochloric acid on titanium hydroxide. It has now been

found that this compound is colourless if the ether employed is from peroxide.

**Gravimetric Estimation of Vanadium as Silver Vanadate.** PHILIP E. BROWNING and HOWARD E. PALMER (*Amer. J. Sci.*, [iv], 30, 220—223).—Experiments made to determine the conditions under which vanadium can be estimated gravimetrically as a vanadate show that the precipitate formed by the addition of a nitrate to a neutral solution is of constant composition, corresponding with the meta-vanadate. From solutions acidified with acetic acid a silver salt of variable composition is precipitated.

**Application of Potassium Ferricyanide in Alkaline Solution to the Estimation of Vanadium and Chromium.** HOWARD E. PALMER (*Amer. J. Sci.*, 1910, [iv], 30, 141—145).—A continuation of the previous paper on this subject (this vol., ii, 516).

**Estimation of Vanadium.**—The vanadate (about 0.1 gram present as an ammonium salt) is acidified with hydrochloric acid and reduced to the blue compound by passing a current of sulphur dioxide. The solution is then boiled in a current of carbon dioxide to expel the traces of the sulphur dioxide. When cold, a solution of potassium ferricyanide is added in quantity at least ten times that theoretically required, followed by 6 grams of potassium hydroxide. After diluting to 100—125 c.c., the vanadic acid is removed by adding a solution of barium hydroxide, and the liquid is filtered through an ashless filter. The filtrate and washings are then acidified with hydrochloric acid, and the ferrocyanide formed in the reaction is titrated with potassium permanganate. Two mols. of ferrocyanide = two atoms of vanadium.

**Estimation of Chromium.**—The process worked out by Bolland and Luchmann (*Abstr.*, 1909, ii, 187) gives good results if at least fifteen times the theoretical quantity of ferricyanide is used and a stronger potassium hydroxide solution is added. In this process chromium is removed before the titration as barium chromate. After acidifying with hydrochloric acid, an excess of permanganate is added and this is titrated in turn by means of  $N/20$ -ferrocyanide in presence of a trace of a ferric salt, the end point being indicated by appearance of a green coloration.

**Estimation of mixed Vanadium and Chromium.**—About 0.2 g. of the mixed compounds, both in the higher state of oxidation, dissolved, and the solution is divided into two equal portions. In one of these the salts are reduced by means of sulphur dioxide as directed, and a sufficient excess of potassium ferricyanide and potassium hydroxide is added. Both vanadate and chromate are then removed by means of barium hydroxide, and the filtrate is acidified with hydrochloric acid. The solution is then titrated with potassium permanganate as in the case of chromium.

The second portion is titrated for vanadium only, as follows: the solution, measuring about 100 c.c., are added 10—15 c.c. of glacial acetic acid and then hydrogen peroxide. On boiling, the chromium is reduced to oxide, whilst the vanadium is not affected. A solution of lead acetate is added, which causes a precipitate of lead vanadate.

becomes more compact when the liquid is heated to boiling. The precipitate is collected on asbestos, washed thoroughly, and dissolved in aqueous potassium hydroxide. The lead is then removed by adding excess of sulphuric acid, and the vanadium reduced by passing a current of sulphur dioxide. After boiling in a current of sulphur dioxide, the vanadium is titrated with permanganate. The amount of permanganate required for the oxidation of the tin is then found by difference.

L. DE K.

#### Separation of Antimony and Tin by Distillation.

LM PLATO (*Zeitsch. anorg. Chem.*, 1910, 68, 26—47).—Antimony may be completely separated from tin by distillation of its stannous chloride, the tin being fixed by means of phosphoric acid. The boiling point of the mixture is best raised by the addition of sulphuric acid. A glass Kjeldahl flask is used, provided with a rubber stopper, through which pass a thermometer, a tap-funnel with stem reaching to the bottom of the flask and fitted with a side arm, and a gas delivery tube connected to a condenser. The lower end of the thermometer is bent, and reaches to the bottom of the receiver. A water tube forms a reflux condenser for this receiver.

A substance containing tin and antimony, such as the mixture of stannous chloride and antimony trichloride, is dissolved in 6 c.c. of concentrated sulphuric acid, and added to the flask together with 7 c.c. of phosphoric acid, D 1.70. After cooling, 10 c.c. of hydrochloric acid are added through the tap-funnel. About 50 c.c. of hydrochloric acid are then placed in the receiver, and the apparatus is connected. During the first heating, sulphur dioxide is led into the flask, and the reflux condenser is cooled with a draught. When the temperature reaches 155—165°, it is kept constant by adding fuming hydrochloric acid at the rate of 5 drops a minute. The distillation lasts one and a-half hours, and the whole of the antimony is then contained in the receiver. It is separated by any of the usual methods.

The tin remaining in the flask may now be distilled into a receiver containing fuming hydrochloric acid. The tap-funnel is filled with a solution of stannous chloride in fuming hydrochloric acid, and 6 c.c. of concentrated sulphuric acid are introduced into the flask. Instead of carbon dioxide, a current of sulphur dioxide is passed through the liquid during the distillation, and the temperature is kept constant at 190°. After an hour, all the tin is present in the receiver as stannous chloride. Sulphur dioxide is then removed by a current of sulphur dioxide, the receiver being heated.

Antimony is best estimated as the trisulphide, and tin by precipitation as stannous sulphide together with a mercury salt, in order to yield a precipitate which is readily filtered, finally igniting to stannic oxide. If arsenic is also present, it is best to distil the solution in fuming hydrochloric acid so as to drive both arsenic and antimony over. After adding 5 grams of tartaric acid to the distillate, it is distilled in a current of carbon dioxide, when all the arsenic passes over. The distillations may be combined by using a receiver, containing fuming hydrochloric and tartaric acids, heated so that the arsenic distils over into a second receiver. Lead is obtained directly as sulphate on

diluting the residue in the distilling flask, and copper may then be estimated electrolytically in the filtrate. C. H.

**Electric Combustion Furnace for Methane Estimation.** J. AUGUST FRIES (*J. Amer. Chem. Soc.*, 1910, 32, 949—953).—An electric combustion furnace has been devised for the estimation of the combustible gases, chiefly or wholly methane, excreted by cattle in the course of respiration calorimeter experiments. The quantity of gas taken for analysis from the respiration calorimeter chamber amounts to 3.5 litres per minute. This volume passes through the combustion tube in which the combustible gases are oxidised, platinum being serving as a catalyst.

The combustion tube is a copper tube of 20 mm. internal diameter and 3.35 metres long; the portion heated is protected by a nickel-plated brass tube which fits loosely over it. The outside box supports for the tube are constructed of asbestos board, three-quarters of an inch thick. The resistance coils are wound on three quartz tubes 37 mm. internal diameter and 70 cm. long. A full description of the furnace is given in the original.

This electric furnace is to be preferred to the gas furnace, as it gives a more uniform heat, can be easily regulated, and obviates the danger of the air supply of the respiration calorimeter becoming contaminated with combustible gases. E. C.

**Condensation of Petroleum and its Distillates with Methylal and Sulphuric Acid.** V. F. HEAR (*Chem. Zeit.*, 1910, 34, 893—894).—Nastukoff's formalin process for the estimation of the hydrocarbons in petroleum which form condensation products with methylaldehyde (*Abstr.*, 1904, i, 80) does not yield concordant results; the product is partly soluble in chloroform. Methylal is a more sensitive reagent for the purpose; by it 0.05 vol. % of benzene is detected, whereas formalin only indicates the presence of 5% of benzene.

The reaction with methylal depends largely on the temperature. A mixture of 5 grams of Baku spindle oil, D 0.900, and 10 gram methylal, cooled by water, is treated with 10 c.c. of concentrated sulphuric acid in a fine stream; when cold the mixture is poured into 200 c.c. of water, and is neutralised with ammonium hydroxide. The precipitate is collected on several layers of filter-paper, dried and washed with water and light petroleum, and is again dried at 100°; the product is a brownish-black substance (C 75.86, H 10.4, S 6.8) which is soluble in chlorobenzene; yield 7%. When the reaction is carried out without cooling, and the mixture is heated on the water bath before being poured into water, the purified product is a dark brown powder (C 68.94, H 7.12, S 7.19%), which is insoluble in chlorobenzene and the usual solvents; yield 26%. A rapid volume modification of the process, which yields relative results, and is suitable for the detection of the adulteration of light oil with deodorized Surachany crude oil, and of benzene with cheap tar oils, is as follows: Two c.c. of the oil and 4 c.c. of methylal, dissolved in 10 c.c. of light petroleum, b. p. 50° (which does not react with methylal), are placed in a graduated stoppered cylinder, treated

with 2 c.c. of sulphuric acid, and vigorously shaken for one hour; after half an hour, the volume of the precipitate, which has settled at the bottom of the cylinder, is read. C. S.

of the Halogen Compounds of the United States Pharmacopoeia with Special Reference to Thymol Iodide. ELVOVE (*Amer. J. Pharm.*, 1910, 82, 403-409).—It is deemed desirable that a general process for the estimation of halogen compounds should be inserted in the United States Pharmacopoeia, and for this purpose the method described by Wallis (1906, ii, 255) or that of Self (Abstr., 1907, ii, 657) is deemed suitable. Thymol iodide is particularly difficult to decompose quantitatively (Gane and Webster, Abstr., 1909, ii, 613), but now that the following modification of Self's process gives good results.

The iodide (0.1 to 0.5 gram) is mixed with ether (10 c.c.), sodium hydroxide in alcohol (20 c.c.), and zinc dust (2 grams), and under a reflux apparatus during one hour. Glacial acetic acid and water (200 c.c.) are then added, and the mixture again refluxed one hour. The reflux apparatus is washed out into the flask and the contents of the latter filtered and the filter washed with ether (30 c.c.). To the filtrate a definite amount of  $N/10$ -silver solution is added, in excess of about 5 c.c. The mixture is allowed to stand during ten minutes, 50 c.c. of 10% nitric acid added, and the solution again boiled during five minutes. The filtrate from this with 50 c.c. of hot water is cooled, and the excess of silver is precipitated by standard thiocyanate, using 5 c.c. of a 10% solution of potassium ferric alum as indicator. Chlorine in the compound can be determined gravimetrically from the weight of the silver precipitate. T. A. H.

$\alpha$ -Naphtholsulphuric Reaction for Dextrose. LASZLÓ VON SZÉKELY (*Zeitsch. physiol. Chem.*, 1910, 68, 88-92. Compare *ibid.*, 1888, 863).—Concentrated sulphuric acid added to a solution of dextrose and  $\alpha$ -naphthol produces a violet ring where the two meet.

The green coloration observed by Goldschmidt (this vol., ii, 555), in testing urines is probably not due to glycuronic acid, but to nitroses or nitrites present in the urine. J. J. S.

New Method for Estimating Sugar in Urine. K. A. LEBALCH and J. LINDBERGH (*Biochem. Zeitsch.*, 1910, 27, 273-295).—An alkaline solution of safranin and other dyes is decolorised by dextrose and other carbohydrates. For quantitative purposes equal volumes of a solution of safranin (1 in 10,000) and potassium hydroxide (1 in 100) are mixed. Two c.c. of this mixture, or more if the quantity of sugar in the urine is large, are mixed with a known number of drops of a sugar solution, and the mixture is warmed on a water-bath. The amount of sugar is estimated by ascertaining the number of drops which are required just to decolorise the alkaline mixture, which can be standardised by a sugar solution. The authors state that the method has the advantage over other methods in that a preliminary separation of proteins is unnecessary, and that the

reduction due to substances in the urine other than sugars is about one-quarter of that found in the Bing-titration method. The authors also give the results of a large number of sugar estimations in normal and pathological urines. The reagents employed deteriorate on keeping. S. B.

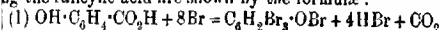
**New Reactions for Salicylic Acid.** C. REICHARD (*Pharm. Ztg.* 1910, 51, 743—749).—Numerous new reactions for salicylic acid are communicated. Of the more characteristic tests, the following are the most important. A pinch of titanous acid is moistened with salicylic acid and heated for a short time; it is not necessary to effect solution. A little salicylic acid is now added, and the whole set aside for 24 hours. If now a drop of aqueous potassium hydroxide is allowed to come in contact with the mixture, a fine orange-red coloration is noticed. Conversely, the test may be used for the detection of titanous acid.

A mixture of salicylic acid and copper sulphate moistened with hydrochloric acid when exposed to the air loses its green color. After some days a reddish-violet coloration appears, resembling the biuret reaction for albumin. A concentrated solution of potassium ferricyanide turns dark green when mixed with salicylic acid; on adding a drop of strong aqueous potassium hydroxide, the liquid becomes a dark green bluish-black, which disappears on shaking; the color then changes to a slightly green brownish-yellow. L. DE

**A Source of Error in the Detection and Estimation of Salicylic Acid.** HENRI PELLET (*Ann. Chim. anal.*, 1910, 302—305).—Attention is drawn to the fact that salicylic acid is a normal constituent of many fruits, etc. When the presence of salicylic acid is detected in an article of food or in a beverage, it is necessary to estimate the quantity present in order to ascertain whether the sample contains added salicylic acid. The amount present naturally, for instance in wine, is about 0.001 gram per litre, whilst it is necessary to add from 0.040 to 0.060 gram per litre before the acid has effective preservation action. The substance discovered by Bücke (vol. i, 225) may also be mistaken for salicylic acid. W. P.

**Estimation of Salicylic Acid in Jams, etc.** TH. VON FRIEDBERG (*Zeitsch. Nahr. Genussm.*, 1910, 20, 63—70).—The process described is a modification of that proposed by Harry and Mum (Abstr., 1905, ii, 426); this method is considered to be inaccurate owing to the fact that a portion of the salicylic acid volatilises during the distillation of the ether, that the lead precipitate contains salicylic acid, that three extractions with ether are insufficient to remove all the salicylic acid, and that the latter is contaminated with fruit acids which interfere with the colorimetric estimation of salicylic acid. The details of the modified process are as follows: Fifteen grams of the sample are mixed with 50 c.c. of warm water, the mixture is neutralised with *N*-sodium hydroxide solution, and treated with 10–15 c.c. of sodium citrate solution, a being the quantity of *N*-sodium hydroxide solution required for the neutralisation.

The sodium citrate solution is prepared by neutralising 35 g. of citric acid with sodium hydroxide, and diluting the solution to a volume of 500 c.c. The mixture is now treated successively with 10 c.c. of basic lead acetate solution, D1.24, 10 c.c. of *N*-sodium hydroxide solution, 5 c.c. of *N*-hydrochloric acid, and 40 c.c. of saturated sodium chloride solution. The addition of these salts liberates salicylic acid being retained in the lead precipitate formed. The whole mass is now diluted to a volume of 100 c.c., filtered, and the filtrate is acidified with 3 c.c. of 20% hydrochloric acid and shaken out with five successive quantities of 50 c.c. of ether. The ether extracts are then rendered alkaline by the addition of 10 c.c. of *N*-sodium hydroxide solution, and the ether is removed by distillation. The residual solution is diluted with water to a volume of 50 c.c., acidified with 7 c.c. of 20% hydrochloric acid, and a measured excess of *N*/50-bromine solution is added. (This solution is prepared by dissolving 0.57 gram of potassium bromate and 1.66 grams of potassium bromide in 1 litre of water). After the reaction has proceeded for five minutes, 0.5 c.c. of 10% potassium iodide solution is added for every 10 c.c. of the bromine solution used, and the liberated iodine is titrated with *N*/50-thiosulphate solution. The bromine and thiosulphate solutions must be titrated against each other under the same conditions as to dilution, acidity, etc., as in the actual estimation. 0.00046 c.c. of *N*/50-thiosulphate solution corresponds with 0.00046 g. of salicylic acid. The reactions taking place in this method of estimation of the salicylic acid are shown by the formulæ:



(2)  $\text{C}_6\text{H}_2\text{Br}_8 \cdot \text{OBr} + 2\text{KI} = \text{C}_6\text{H}_2\text{Br}_8 \cdot \text{OK} + \text{KBr} + \text{I}_2$ . The excess of iodine added is also titrated as iodine, and the difference in the volumes of thiosulphate solution used in the actual estimation and blank titration gives the amount of salicylic acid present. It was found by experiment that the process yields only 90% of the salicylic acid actually present, and that jams contain substances which combine with bromine-additive compounds, the quantity of these substances being about 0.05 gram per kilogram of jam. The apparent quantity of salicylic acid, *S*, in the sample is found from the equation:  $S = 0.046 \times T \times a$ , where *T* is the titre of the thiosulphate solution, and *a* the quantity of thiosulphate solution used for the estimation of the sample. The actual quantity, *x*, is obtained from the equation:  $x = S - 0.05 + 0.1(S - 0.05)$ . The limit of error of the process is 0.01%.

W. P. S.

**Extraction Apparatus.** GEORGE S. WALPOLE (*Chem. News*, 1910, 129—130).—A modified Soxhlet apparatus is described in which there are no corks, rubber stoppers, or ground-in joints. The extraction flask is provided with a flange in which the outer part of the extraction part of the apparatus rests, mercury being placed in this space so as to form a mercury seal. An inner tube is placed in the extraction portion of the apparatus, and in this is fitted a tube for holding the extraction thimble or cartridge; the lower part of the inner tube is provided with a siphon tube as in the Soxhlet apparatus. A condenser is attached by means of a blown-in joint to the top of



the outer tube. The extraction thimble may be dispensed with, if desired, and the material to be extracted packed in the inner tube itself.

**Fat Extraction Apparatus.** WILLIAM CLACHER (*Analyst*, 1909, 349).—The apparatus consists of a short glass tube, the lower end of which is closed by a linen cap; the substance to be extracted is placed in this tube, which is then suspended, open end upwards, in a necked flask by means of threads. The flask contains a suitable solvent such as ether, and is placed on a water-bath. The vapour of the boiling solvent is condensed on a test-tube inserted through the neck of the flask, and the condensed liquid drops into the test-tube, closing the flask, and the condensed liquid drops into the test-tube and percolates the contents. The test-tube is provided with a supply of cold water, and a small opening in the cork of the test-tube vents excessive pressure of vapour in the latter. A small hole on the side of the extraction tube near the top allows the condensed liquid to pass from the tube into the flask should the rate of condensation exceed the speed at which the solvent percolates the substance.

**Detection and Estimation of "Saccharin" in Foods containing Fats, Starch, and Proteins.** MASSIMO TORTELLI and E. R. (*Ann. Falsif.*, 1910, 3, 313—320).—The following procedure is recommended for separating "saccharin" from foods, and for removing substances extracted along with the "saccharin." The sample is mixed with sand and a small quantity of calcium hydroxide; the foods are evaporated to dryness after the addition of the sand (calcium hydroxide), and the mixture is extracted several times with boiling alcohol, a quantity of saturated sodium chloride solution being added with each quantity of alcohol. The alcoholic extracts are then filtered, and the filter is washed with a mixture of alcohol and sodium chloride solution. The filtrate is evaporated to a volume of about 70 c.c., 15 c.c. of saturated sodium chloride solution are added, and the mixture is shaken several times with light petroleum to remove fatty substances. The residual solution is next heated to expel all the remaining alcohol, then acidified with sulphuric acid, and the "saccharin" is extracted with a mixture consisting of equal volumes of ether and light petroleum. On evaporation of the separated solvent, the "saccharin" is obtained as a crystalline residue. A substance similar to "saccharin" is sometimes present in foods, namely, "dulcin" or "sacrol" (*p*-phenetolecarbamide), which is extracted from the food along with "saccharin" as described above, but it is only slightly soluble in the light petroleum-ether mixture, and is quite insoluble in light petroleum; it is soluble in ether alone. "Saccharin," m. p. 223°, may be distinguished from "dulcin," m. p. 173°, from the fact that the former gives a faint violet coloration when heated with mercuric nitrate solution; this coloration becomes more intense on addition of a trace of lead peroxide.

Wines and the Acrylic Fermentation of Glycerol. DENET (*Compt. rend.*, 1910; 151, 518—520. Compare this vol., —Denigès' reaction (Abstr., 1909, ii, 272, 273) may be used to recognise the presence of acetaldehyde in bitter wines, the wine being treated successively with bromine, baryta water, and sodium hydroxide to convert the aldehyde into dihydroxyacetone.

The amount of acetaldehyde found gives no indication of the amount of acrylaldehyde formed, since a portion undergoes conversion into acrylic acid and resinous products, the latter giving rise to the characteristic odor.

W. O. W.

[French] Official Method for Titrating Pyrimidone. REMAIRE (*Ann. Chim. anal.*, 1910, 15, 307—308).—The author draws attention to an error in the directions prescribed by the French Pharmacopoeia for the titration of pyrimidone; 5 grams of the sample, instead of 0.5 gram, should require not less than 20 c.c. of *N*-acid for neutralization.

He also points out that the titration, using methyl-orange as indicator, yields results which vary slightly according to the dilution, the nature of the solution, and quantity of methyl-orange added.

W. P. S.

Determination of Creatinine. PETER RONA (*Biochem. Zeitsch.*, 1910, 37, 348).—Folin's colorimetric method can be advantageously applied to meat-extracts, urine, etc., if the pigment be first removed with sodium hydroxide, which does not adsorb the creatinine. S. B. S.

Determination of Ornithine in the Cleavage Products of Lysine. ALBRECHT KOSSEL and FA. WEISS (*Zeitsch. physiol. Chem.*, 1908, 160—164. Compare Abstr., 1909, i, 542).—In the hydrolysis of lysine, ornithine can, after the removal of histidine and proline, be isolated readily as picrate, aurichloride, or most readily as benzoyl derivative. In the presence of lysine, it is most readily isolated as the picrate, as this is much more readily soluble in water, especially in methyl alcohol, than lysine picrate.

Ornithine monopicrate (Schulze and Winterstein, Abstr., 1902, i, 103, has m. p. 203—204°, and contains 11H<sub>2</sub>O. *dl*-Ornithine monopicrate (Fischer and Raske, Abstr., 1903, i, 863; Riesser, Abstr., 1903, 78) forms large, triclinic crystals and is anhydrous (Riesser 1.5H<sub>2</sub>O).

*dl*-Ornithine dipicrate, C<sub>5</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>·2C<sub>6</sub>H<sub>3</sub>O<sub>7</sub>N<sub>3</sub>, has m. p. 195°, and does not appear to be identical with the products described by Fischer and Raske and by Riesser, and is formed to a slight extent when the monopicrate is recrystallised.

*Ornithine dipicrolonate*, C<sub>5</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>·2C<sub>6</sub>H<sub>3</sub>O<sub>5</sub>N<sub>3</sub>, has m. p. 236°.

One hundred c.c. of methyl alcohol dissolve 4.2—4.5 grams of *dl*-ornithine dipicrate and 2.5—3 grams of *dl*-monopicrate, but only 0.4 gram of *d*-ornithine monopicrate.

The process of separation from lysine works best with the inactive *dl*-isomer, and when *l*-ornithine is present, it is advisable to racemise the mixture by means of concentrated sulphuric acid before carrying out the separation.

J. J. S.

**Reactions of Alkaloids with Hydrogen Peroxide.** SHAER (*Arch. Pharm.*, 1910, 248, 458—462).—A description of the colour reactions of many of the alkaloids with a reagent prepared by mixing 1 volume of Merck's 30% "perhydrol" with 10 volumes of pure sulphuric acid. As a rule, the colour reactions are more characteristic than others already known. Quinine, however, produces, even in minute quantities, an intense citron-yellow to yellow coloration. Nicotine and hydrastine produce intense red colorations.

**The Volumetric Estimation of Hydroferro- and Hydrocyanic Acids.** ERICH MÖLLER and OTTO DIEFENTHALER (*Z. anorg. Chem.*, 1910, 67, 418—436. Compare Mecklenburgh, *ibid.*, ii, 761).—The titration of ferrocyanides with permanganate, the accuracy of which has been called in question, gives good results when carried out by using a solution containing about 1 gram of the cyanide in 150—200 c.c. of water, adding 20 c.c. of sulphuric acid (1:4), and titrating with  $N/20$ -potassium permanganate until the colour becomes yellowish-red. Ferrocyanides are estimated in the same way after reduction with ferrous sulphate in alkaline solution.

The estimation of hydroferrocyanic acid by addition of a solution of iodine and titration with thiosulphate in alkali hydrogen carbonate solution is inaccurate, owing to the action of the carbonate on the iodine (Foerster and Gyr, *Abstr.*, 1903, ii, 209), and the use of arsenious acid does not give better results.

Ferrocyanides may be accurately titrated in neutral solution containing about 0.7 gram in 50 c.c. of water, by adding 3 grams of potassium iodide and 1.5 grams of pure zinc sulphate, and titrating with thiosulphate and starch immediately after shaking. C. H.

**Chemical Tests for Blood.** PHILIP A. KOBER, W. G. LIND, and J. T. MARSHALL (*J. Biol. Chem.*, 1910, 8, 95).—Most observers recognise that whilst substances other than blood give a positive reaction with the guaiacum and similar tests, a negative result is not proof of its absence. This must be corrected, for solutions of tea, acid or extracts of tea or coffee prevent the occurrence of the reaction when a small amount of blood is present in the gastric contents. Using the Ewald-Ross test meal, water and not tea should therefore be given. W. D.

**A New Colorimeter and its Application to the Estimation of the Colouring Matter of Blood, Iron, Indican, Creatinine.** WILHELM AUTENRIETH and JOHANN KORSICKE (*Munch. med. Woch.*, 1910, No. 19, 1—10).—The colorimeter described and figured is chiefly designed for measurement in physiological chemistry. Its advantages are that measurement is made by displacement of the comparison vessel, so that no dilution is necessary; the vessels have parallel walls, and are thus more satisfactory than circular tubes, and, further, a very accurate comparison of the two colours is rendered possible by the use of a Helmholtz double plate, which abolishes the line of separation.

the comparison solutions employed are stable and readily

the determination of the proportion of colouring matter and of iron and of indican and creatinine in urine, by means of the method described in detail, the standard methods described by observers being used in each case. In the course of the experiments it was found that the amount of creatinine secreted in the one day varied from 1.7 to 2.3 grams.

G. S.

#### Reagent for Urobilin, Urobilinogen, and Blood.

FLORENCE (*J. Pharm. Chim.*, 1910, [vii], 2, 160).—The test of colour, which occurs naturally in hæmaphysic urines and is expedited by mixing from 2 to 3 c.c. of the urine with an equal volume of a solution of zinc acetate (7.5 grams) in a mixture of equal parts of pyridine, alcohol, and chloroform. On shaking and allowing to stand, the lower layer remains colourless if no pigments are present, but fluoresces green if urobilin is present, gradually fluoresces green if urobilinogen is present, and eventually fluoresces green if urobilinogen is present, and is rose- or cherry-red if blood occurs in the urine. The intensity of the colour may be used to estimate approximately the amount of pigment present. The solutions show well marked bands.

T. A. H.

#### Separation of Hæmaphysic Pigments.

ALBERT FLORENCE (*J. Pharm. Chim.*, 1910, [vii], 2, 161—163).—The urine is placed in a test-tube, and an equal volume of acetone added and granular ammonium sulphate to saturation, and the mixture shaken. The acetone dissolves the pigments, and separates as a layer, from which the aqueous liquor may be drawn off. The solution is then dried by means of granular ammonium sulphate, and on evaporation in a tared vessel leaves, as a residue, the hæmaphysic pigments. From this, chloroform removes urobilin, leaving a red acid deliquescent pigment, soluble in alcohol, which does not give a band spectrum and does not fluoresce with zinc salts.

T. A. H.

Reaction of Blood with Guaiacum Resin with the Aid of Potassium Perborate. BRUNO BARDACH and SIEGMUND SILBERSTEIN (*Chem. Zeit.*, 1910, 34, 814—815).—To 5 c.c. of the liquid to be tested (urine, for instance) are added a few drops of cold saturated, prepared tincture of guaiacum, and then 1 c.c. of powdered potassium perborate, followed by 10 c.c. of 30% acetic acid. After shaking, the test-tube is sharply inclined, and a little alcohol is carefully added over the surface of the liquid. If blood is present, a blue or green coloration will be noticed at the place of contact within minutes.

Guaiacum resin which has turned greenish or bluish-green either on the surface or throughout the mass should not be used.

L. DE K.

Dilute Reaction for Glue. EUGEN SCHMIDT (*Chem. Zeit.*, 1910, 34, 839).—The reagent consists of a solution of 3 grams of

ammonium molybdate in 250 c.c. of water, and 25 c.c. of nitric acid D 1.2.

This reagent is particularly suited for the detection of gelatin in fabrics. The sample is boiled with water, the solution is concentrated on the water-bath, and then treated with the reagent, which will give a heavy white precipitate. Other substances used in dressing fabrics, such as gum arabic, decoction of linseed, etc., only give a turbidity but no characteristic precipitate.

**Urine Colorations.** C. J. REICHARD (*Pharm. Zeit.*, 1908, 538).—When applying the nitric acid boiling test to urine, the author prefers using a nitric acid, D 1.2. At first this is added until the urine has a decided acid reaction, and then during boiling more acid is added, until the coloration no longer increases. If acid of greater strength is used, the coloration is in danger of being destroyed.

The colour reaction is due, not only to the action of the acid on existing colouring matters of the urine, but also to carbohydrates, mucin if present. The colouring matters formed, including the carbohydrates, may be for the greater part removed by shaking with alcohol.

**A Simple Estimation of Trypsin and the Law of Trypsin Fermentation.** ALEXANDER PALLADIN (*Pflüger's Archiv*, 1910, 337—364).—A protein such as fibrin or glue is dyed before immersion in the trypsin solution. As fermentation proceeds, the solution becomes coloured proportionately to the amount of protein dissolved. And an estimation of the amount of trypsin present is effected by colorimetric comparison with the result of a similar fermentation by a known amount of trypsin in the same solution. The dyeing of the protein is best effected with "spirit blue shade" (Farbenfabriken vorm. F. Bayer & Co.). The method has also been employed to determine the law according to which trypsin fermentation proceeds, as this has been the subject of conflicting statements. It has been found that in the case of the fermentation of a solid protein, or of glue, when care is taken that the surface contact of solid and solution always remains the same size, the amount fermented is nearly proportional to the cube root of the square of the amount of ferment present. When the protein is powdered or enclosed in Mett tubes, the amount fermented is more nearly proportional to the square root of the amount of ferment in solution, whilst when the protein is in solution the amount hydrolysed is simply proportional to the quantity of ferment present. The result confirms that of Gross (compare Abstr., 1908, 231), and is obtained by his method.











